J. Chem. Eng. Data **2000,** *45,* 953−960

Measurement and Prediction of the Monocarboxylic Acids Thermochemical Properties

S. P. Verevkin

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18051 Rostock, Germany

The standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ or sublimation $\Delta_{cr}^g H_m^\circ$ of 2-methylpropanoic, butanoic, 2-methylbutanoic, 3-methylbutanoic, pentanoic, 2,2-dimethylpropanoic, 3,3-dimethylbutanoic, hexanoic, heptanoic, and octanoic acids were measured by the transpiration method. The enthalpies of vaporization $\Delta_l^g H_m^\circ$ of ethanoic, propanoic, 2-methylpropanoic, and butanoic acids were measured using correlation gas chromatography. The enthalpies of the phase transitions of 2,2-dimethylpropanoic acid were measured using differential scanning calorimetry. The values of $\Delta_l^g H_m^\circ$ of the compounds studied were taken as a basis for the development of a group-additivity predictive scheme. The standard molar enthalpies of formation $\Delta_f H_m^\circ$(g) at the temperature $T = 298.15$ K of monocarboxylic acids were derived using the data for $\Delta_f H_m^\circ$(l or cr) from the literature and the present results for the enthalpies of vaporization or sublimation. The improved group-contribution method was used for the estimation of the gaseous enthalpies of formation of monocarboxylic acids.

Introduction

Rapid progress in computer techniques promises the calculation of reliable values of the gaseous enthalpies of formation $\Delta_f H_m^\circ$(g) of organic compounds. Indeed, for the practical application in chemical technology, the enthalpies of formation in liquid or crystalline state $\Delta_f H_m^\circ$(l or cr) are of high importance. To derive values of $\Delta_f H_m^\circ$(l or cr) from $\Delta_f H_m^\circ$(g) are required the values of enthalpies of vaporization $\Delta_l^g H_m^\circ$ or sublimation $\Delta_{cr}^g H_m^\circ$. Thus, experimental measurements of the enthalpies of vaporization and sublimation and development of the prediction method are of increasing interest.

Peculiarities of the monocarboxylic acid thermodynamic properties have attracted experimental and theoretical interest for more than one hundred years. There are abundant vapor pressure measurements of carboxylic acids in the literature (Jasperson et al., 1989; Andereya and Chase, 1990). However, enthalpies of vaporization/sublimation at the reference temperature 298.15 K of the lower monocarboxylic acids were reported only twice (Konicek and Wadsö, 1970; de Kruif and Oonk, 1979). Very accurate enthalpies of vaporization were measured by Konicek and Wadsö (1970) using calorimetry. However, these values are referred to the process RCOOH(liquid, 298.15 K) = RCOOH (gas, equilibrium mixture monomer−dimer at saturation pressure, 298.15 K). For the correct recalculation of these enthalpies of vaporization for the process RCOOH(liquid, 298.15 K) = RCOOH(gas, monomer, 298.15 K), additional information concerning values of ΔH_{diss} (enthalpy of dissociation of dimeric carboxylic acid in gaseous state) is required. The gas-phase equilibrium between monomeric and associated dimer molecules has been studied experimentally for the carboxylic acids by several techniques, and a considerable body of data has been accumulated (Tsonopoulus and Prausnitz, 1970; Jasperson et al., 1989). Unfortunately, analysis of the data for ΔH_{diss} of monocarboxylic acids has detected a very large scatter of the values, having broad boundaries of (5−7) kJ·mol^{-1} (Andereya and Chase, 1990). Thus, the precise vaporization enthalpies measured by Konicek and Wadsö (1970) are less precise when corrected for the monomeric vapor. The only direct measurements of the vaporization enthalpies of monocarboxylic acids were reported by de Kruif and Oonk (1979). They used combined torsion- and weighing-effusion techniques (Calis-Van Ginkel et al., 1978; de Kruif and Oonk, 1979) for the simultaneous determination of the total vapor pressure and the molar mass of the vapor. However, the accuracy of their enthalpies of vaporization was generally not better than ±3.0 kJ·mol^{-1}. The inaccuracy which is associated with the techniques employed does not allow for a reliable comparison with the enthalpies of vaporization $\Delta_l^g H_m^\circ$(298.15 K) available from the literature and does not allow the development of predictive schemes for their calculation. In such a situation, we have been encouraged to redetermine the enthalpies of vaporization of some linear monocarboxylic acids and to extend the study with emphasis on the branched representatives of this homological series (see Figure 1). Bearing in mind the strong association of carboxylic acids in the vapor phase, which depends on the number of carbon atoms in the acid, two different methods were used to measure enthalpies of vaporization. The transpiration method (Cox and Pilcher, 1970) was used to determine enthalpies of vaporization or sublimation of carboxylic acids with carbon chain length C_4−C_8. This method has already been applied successfully for associated compounds such as alcohols (Verevkin, 1998a), phenol, and alkylphenols (Verevkin, 1998b). The enthalpies of vaporization of the lower carboxylic acids C_2−C_3 were determined using the so-called “correlation gas chromatography method” (Chickos et al., 1995; Verevkin and Heintz, 1999). This method correlates the gas-chromatographic behavior (retention time) of a compound of interest with the net of the retention times of some standard compounds with known enthalpies of vaporization, already referred to the process RCOOH(liquid, 298.15 K) ↔ RCOOH(gas, monomer, 298.15 K). The derived values of $\Delta_l^g H_m^\circ$ together with

---

* E-mail: sergey.verevkin@chemie.uni-rostock.de.

10.1021/je990282m CCC: $19.00 © 2000 American Chemical Society
Published on Web 06/02/2000

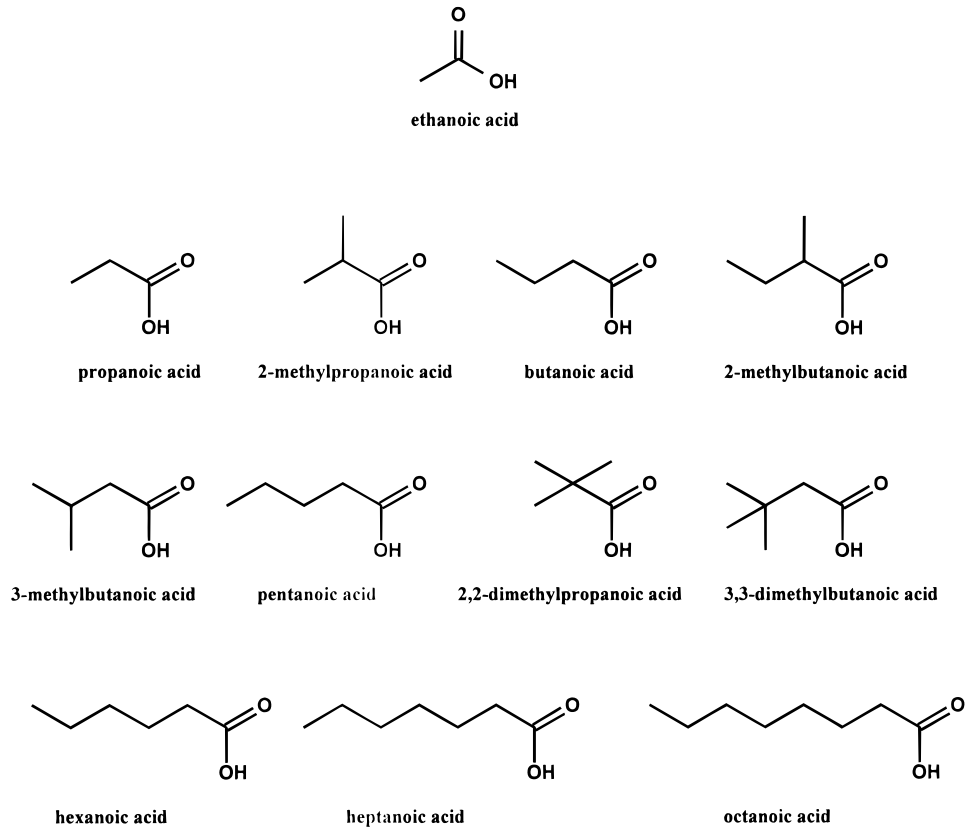

Figure 1. Structures of the investigated carboxylic acids.

the values available from the literature were used to develop a group-additive scheme for the prediction of the enthalpies of vaporization of the monocarboxylic acids.

The thermochemistry of monocarboxylic acids in the condensed state is well established. Reliable values $\Delta_f H^\circ_m$(l or cr) are available from Pilcher (1992). Some new results for $\Delta_f H^\circ_m$(l or cr) have been reported recently for the branched carboxylic acids by Ribeiro da Silva et al. (1999). To obtain $\Delta_f H^\circ_m$(g) we used the values of $\Delta_l^g H^\circ_m$ redetermined in this study and the known (Pilcher, 1992; Ribeiro da Silva et al., 1999) values for the enthalpies of formation in the condensed state $\Delta_f H^\circ_m$(l or cr) to derive $\Delta_f H^\circ_m$(g). The group-contribution method was then developed to predict values of the enthalpies of formation of carboxylic acids in the gas phase.

Experimental Section

Materials. Pure Aldrich, Acros, and Merck products (Figure 1), each with a mass-fraction purity of about 0.99, were purified by repeated distillation under reduced pressure. To avoid traces of water, the purified liquid samples were dried over molecular sieves and distilled once more before the experiments. The degree of purity was determined by GLC. No impurities (greater than mass fraction 10^{-4}) could be detected. We used the following equipment: GLC (Carlo Erba Fraktometer Vega Series GC 6000), Hewlett-Packard Integrator 3390A, N_2-flow of 0.333 $cm^3 \cdot s^{-1}$, SE-30 capillary columns of length 25 m and 50 m. The standard temperature program of the GC was $T = 303$ K for 5 min followed by a heating rate 0.167 $K \cdot s^{-1}$ to $T = 523$ K. The melting temperature and enthalpies of fusion and transition of 2,2-dimethylpropanoic acid were determined with a Perkin-Elmer DSC-2C.

Measurements of the Enthalpies of Vaporization by the Transpiration Method. The enthalpies of vaporization of carboxylic acids 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; Verevkin and Heintz, 1999) and has proven to give results in excellent agreement with those of 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 GLC analysis using an internal standard (hydrocarbons n-$C_{11}H_{24}$ or n-$C_{13}H_{28}$). The flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, the flow rate of the nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from the U-tube due to diffusion. On the other hand, the flow rate should not be 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 $cm^3 \cdot s^{-1}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of 0.82 $cm^3 \cdot s^{-1}$. Thus, we carried out the experiments in the flow rate interval (0.26 to 0.52) $cm^3 \cdot s^{-1}$, which has ensured that the transporting gas was in saturated equilibrium with the coexisting liquid (or solid) 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 assuming the validity of the ideal gas law:

$$p = mRT_a/V(N_2)\cdot M \qquad (1)$$

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 ambient temperature. The volume of transporting gas $V(N_2)$ was determined from the flow rate and time measurements. The flow rate was maintained constant with the help of the high-precision needle valve (Hoke, C1335G6BMM-ITA). The accuracy of the volume $V(N_2)$ measurements from the flow rate was established to be ($\pm 0.001\ \mathrm{dm^3}$) with the help of a series of experiments where the volume of nitrogen was measured with a gas-clock or by withdrawing water from the calibrated gasometer. Because the nitrogen stream was measured using a soap bubble flow meter at ambient temperature, this temperature was applied for the calculation of the vapor pressure p according to 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 a function of temperature are shown in Table 1. To derive the standard molar enthalpy of vaporization $\Delta_l^g H_m^\circ(T)$ 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 $b = \Delta_l^g H_m^\circ(T)\cdot R^{-1}$. The observed enthalpies of vaporization $\Delta_l^g H_m^\circ(T)$ 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 the average deviation of the experimental $\ln(p)$ from this linear correlation.

Measurements of the Enthalpies of Vaporization by Correlation Gas Chromatography. The second method used was the method of correlation gas chromatography (Chickos et al., 1995). This method correlates the gas-chromatographical behavior (retention time) of a compound of interest with the net of the retention times of some standard compounds with known enthalpies of vaporization. We used for the measurements the gas chromatograph Carlo Erba Fraktometer Vega Series GC 6000, equipped with the FID and a Hewlett-Packard Integrator 3390A. GLC runs were done isothermally on an SE-30 capillary column of length 25 m or 50 m and diameter 0.32 mm, and the film thickness of the stationary phase was 0.25 μm. Nitrogen was used as a carrier gas at a column-head pressure of 152 kPa. The GLC experiments were performed on two mixtures containing respectively C_2−C_4 and C_5−C_8 carboxylic acids. At each temperature the retention times t_r were corrected with the value for nonretained component (methane). The temperature of the GLC column was maintained constant within ±0.1 K. Depending on the experimental conditions, corrected retention times were generally reproducible to within 1 s. The enthalpies of transfer $\Delta_{sol}^g H_m^\circ$ from a solution of a compound of interest in the stationary phase to the gas phase (Chickos et al., 1995) were obtained in the temperature range (303−378) K for each compound by plotting $\ln(1/t_r)$ versus $1/T$. The slope of this linear correlation $\ln(1/t_r) = a + b/T$ when multiplied by the gas constant, R, gives $\Delta_{sol}^g H_m^\circ$. The linear relationship between $\Delta_{sol}^g H_m^\circ$ and $\Delta_l^g H_m^\circ$ for the structurally related compounds suggests an easy possibility for obtaining the enthalpy of vaporization of an unknown compound.

Enthalpies of Phase Transitions from DSC**.** To derive the enthalpy of vaporization of 2,2-dimethylpropionic acid and to use the value in the correlation gas chromatography, the enthalpy of fusion of this compound was measured with DSC. We determined the enthalpy of the solid-phase transition at the temperature 278.2 K to be $\Delta H_{tr} = (8.11 \pm 0.21)\ \mathrm{kJ\cdot mol^{-1}}$ and the enthalpy of melting at 309.0 K to be $\Delta_{cr}^l H_m^\circ = (2.38 \pm 0.21)\ \mathrm{kJ\cdot mol^{-1}}$. These results are in very good agreement with those of an earlier investigation (Singh and Glicksman, 1990): $\Delta H_{tr} = (8.18 \pm 1.09)\ \mathrm{kJ\cdot mol^{-1}}$ at (278.0 ± 0.2) K and $\Delta_{cr}^l H_m^\circ = (2.27 \pm 0.46)\ \mathrm{kJ\cdot mol^{-1}}$ at 309.09 K. The enthalpy of sublimation measurement for 2,2-dimethylpropionic acid was carried out above the solid-phase transition temperature.

Results and Discussion

Enthalpies of Vaporization from the Transpiration Method. The experimental enthalpies of vaporization $\Delta_l^g H_m^\circ$ or sublimation $\Delta_{cr}^g H_m^\circ$ at $T = 298.15$ K are recorded in Table 1. Because of the deviations from $T = 298.15$ K of the average temperatures of measurement by the transpiration method, the observed values of the enthalpies of vaporization or sublimation of acids (see Table 1) had to be corrected to this reference temperature. The corrections were estimated with the help of the modified "Sidgwick correction":

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

$$\{\Delta_{cr}^g H_m^\circ(\langle T\rangle) - \Delta_{cr}^g H_m^\circ(298.15\ \mathrm{K})\}/(\mathrm{kJ\cdot mol^{-1}}) = (-3.20 \times 10^{-2})\{(\langle T\rangle/\mathrm{K}) - 298.15\} \qquad (4)$$

following the recommendation of Chickos et al. (1993). With these corrections and the measured values of $\Delta_l^g H_m^\circ(T)$ and $\Delta_{cr}^g H_m^\circ(T)$ from Table 1, the standard molar enthalpies of vaporization or sublimation at $T = 298.15$ K were calculated (Table 1). To provide the reliability of the measured values by the transpiration method, some carboxylic acids were investigated twice using different flow rates of carrier gas. For example, the measurement of the enthalpy of vaporization of 3,3-dimethylbutanoic acid was carried out in two runs. The first run, in the temperature range (283.2 to 303.2) K with an N_2 flow of $0.25\ \mathrm{cm^3\cdot s^{-1}}$, gave $\Delta_l^g H_m^\circ = (64.59 \pm 0.74)\ \mathrm{kJ\cdot mol^{-1}}$ at $T = 298.2$ K. The second run, in the range (295.3−325.2) K with a flow rate of $0.50\ \mathrm{cm^3\cdot s^{-1}}$, gave $\Delta_l^g H_m^\circ = (62.23 \pm 0.36)\ \mathrm{kJ\cdot mol^{-1}}$ at $T = 310.2$ K, in good agreement with the first measurement (taking into account the slightly different temperature range of the investigation). The data from both runs were treated together, and the data are listed in Table 1.

Enthalpies of Vaporization from Correlation Gas Chromatography. The experimental results for the temperature dependence of the corrected retention time in the form of the equation $\ln(1/t_r) = a + b/T$ are listed in Table

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

T^a / K	m^b / mg	$V(N_2)^c$ / dm^3	p^d / Pa	T^a / K	m^b / mg	$V(N_2)^c$ / dm^3	p^d / Pa
2-Methylpropanoic Acid[e] $\ln p/\mathrm{Pa} = (28.17 \pm 0.12) - (6710 \pm 34)(T/\mathrm{K})^{-1}$							
278.2	2.70	1.428	56.96	298.2	6.12	0.606	287.5
283.2	3.64	1.236	86.53	303.2	7.41	0.510	411.7
288.2	3.08	0.687	130.0	308.2	6.05	0.287	596.6
293.3	5.74	0.821	200.4				
Butanoic Acid[f] $\ln p/\mathrm{Pa} = (28.58 \pm 0.13) - (7036 \pm 36)(T/\mathrm{K})^{-1}$							
278.2	7.87	8.797	26.69	298.2	7.36	1.436	145.7
283.2	6.83	4.849	41.00	303.2	5.59	0.728	217.5
288.2	5.46	2.457	64.03	308.1	6.81	0.630	305.4
293.3	3.61	1.053	97.95				
3-Methylbutanoic Acid[g] $\ln p/\mathrm{Pa} = (28.65 \pm 0.12) - (7299 \pm 36)(T/\mathrm{K})^{-1}$							
293.4	3.57	2.033	43.21	313.2	3.47	0.408	206.6
298.2	2.74	1.052	63.81	318.1	4.45	0.361	299.3
303.2	2.77	0.699	96.92	323.2	5.94	0.338	427.4
308.2	2.47	0.432	139.5				
2-Methylbutanoic Acid[h] $\ln p/\mathrm{Pa} = (28.83 \pm 0.17) - (7388 \pm 51)(T/\mathrm{K})^{-1}$							
293.5	2.97	1.915	38.19	313.3	4.27	0.542	191.5
298.1	2.33	1.005	56.73	318.2	5.27	0.471	271.9
303.3	1.93	0.526	89.42	323.1	4.49	0.283	385.6
308.2	3.05	0.573	129.7				
Pentanoic Acid[i] $\ln p/\mathrm{Pa} = (28.79 \pm 0.17) - (7582 \pm 61)(T/\mathrm{K})^{-1}$							
283.2	0.672	2.329	7.172	303.2	1.22	0.702	42.41
288.2	0.632	1.308	11.19	308.2	1.45	0.550	64.07
293.2	0.826	1.117	18.11	313.2	1.72	0.439	95.20
298.2	0.695	0.622	27.27				
2,2-Dimethylpropanoic acid[j] $\ln p/\mathrm{Pa} = (29.91 \pm 0.23) - (7497 \pm 66)(T/\mathrm{K})^{-1}$							
278.3	2.77	3.732	18.96	293.3	2.80	0.901	76.40
283.2	2.49	1.994	31.19	298.2	3.02	0.622	118.5
288.3	4.30	2.153	49.36	303.2	4.26	0.598	173.5
3,3-Dimethylbutanoic acid[k] $\ln p/\mathrm{Pa} = (29.18 \pm 0.35) - (7654 \pm 105)(T/\mathrm{K})^{-1}$							
283.2	2.91	7.253	8.824	305.1	2.02	0.752	57.52
288.1	4.77	7.065	14.67	308.4	1.34	0.393	72.93
293.2	1.22	1.280	20.55	310.1	2.09	0.515	86.80
295.3	1.46	1.275	24.74	313.2	3.07	0.526	124.6
298.2	1.43	0.926	33.24	315.1	3.50	0.546	136.9
300.1	1.73	0.998	37.26	320.2	3.27	0.356	195.9
303.2	1.66	0.691	51.55	325.2	3.16	0.238	284.0
Hexanoic Acid[l] $\ln p/\mathrm{Pa} = (29.53 \pm 0.33) - (8227 \pm 103)(T/\mathrm{K})^{-1}$							
297.2	1.91	6.264	6.550	318.1	1.39	0.785	37.82
302.2	3.78	8.384	9.659	323.2	1.30	0.463	59.93
308.1	2.00	2.590	16.53	328.1	1.34	0.330	86.48
313.2	1.60	1.327	25.73				
Heptanoic Acid[m] $\ln p/\mathrm{Pa} = (29.98 \pm 0.32) - (8722 \pm 99)(T/\mathrm{K})^{-1}$							
283.2	0.294	13.015	0.4373	313.2	0.402	0.854	8.968
298.2	0.373	3.541	2.009	318.2	0.494	0.710	13.24
303.2	0.399	2.297	3.315	323.2	0.508	0.479	20.19
308.2	0.265	0.973	5.178	328.2	0.818	0.550	28.29
Octanoic Acid[n] $\ln p/\mathrm{Pa} = (31.80 \pm 0.24) - (9593 \pm 75)(T/\mathrm{K})^{-1}$							
297.4	0.373	10.134	0.6338	323.2	0.745	1.512	8.460
303.2	0.276	4.109	1.154	328.2	1.05	1.354	1.3.34
308.2	0.327	3.088	1.819	333.1	2.38	2.082	19.59
313.2	0.354	1.821	3.345	338.1	1.31	0.736	30.61
318.3	0.442	1.425	5.323	343.1	1.38	0.522	45.31

[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. [e] $\Delta_l^g H_m^\circ$(293.1 K) = (55.79 ± 0.28) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (55.52 ± 0.28) kJ·mol^{-1}. [f] $\Delta_l^g H_m^\circ$(293.1 K) = (58.50 ± 0.30) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (58.23 ± 0.30) kJ·mol^{-1}. [g] $\Delta_l^g H_m^\circ$(308.3 K)= (60.69 ± 0.30) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (61.24 ± 0.30) kJ·mol^{-1}. [h] $\Delta_l^g \mathrm{H}_m^\circ$(308.3 K) = (61.43 ± 0.42) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (61.98 ± 0.42) kJ·mol^{-1}. [i] $\Delta_l^g \mathrm{H}_m^\circ$(298.2 K) = (63.04 ± 0.51) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (63.04 ± 0.51) kJ·mol^{-1}. [j] $\Delta_{cr}^g H_m^\circ$(290.7 K) = (62.33 ± 0.55) kJ·mol^{-1}; $\Delta_{cr}^g H_m^\circ$(298.15 K) = (62.09 ± 0.55) kJ·mol^{-1}. [k] $\Delta_l^g H_m^\circ$(304.2 K) = (63.64 ± 0.87) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (63.97 ± 0.87) kJ·mol^{-1}. [l] $\Delta_l^g H_m^\circ$(312.6 K) = (68.40 ± 0.86) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (69.19 ± 0.86) kJ·mol^{-1}. [m] $\Delta_l^g H_m^\circ$(305.7 K) = (72.52 ± 0.82) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (72.93 ± 0.82) kJ·mol^{-1}. [n] $\Delta_l^g H_m^\circ$(320.2 K) = (79.76 ± 0.62) kJ·mol^{-1}; $\Delta_l^g H_m^\circ$(298.15 K) = (80.96 ± 0.62) kJ·mol^{-1}.

Table 2. Comparison of the $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ Values for the Process RCOOH(liquid, 298.15 K) = RCOOH(gas, monomer, 298.15 K) Obtained by Transpiration and by Correlation Gas Chromatography, and Those Known from the Literature

		25 m SE-30				50 m SE-30					
	$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ [a]			$\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}$	$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ [b]			$\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}$	$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ [c]	$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ [d]	$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ [e]
	kJ·mol^{-1}	*a*	*b*	kJ·mol^{-1}	kJ·mol^{-1}	*a*	*b*	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
ethanoic		1.48	−2744	22.8	50.2	−3.69	−367	3.05	50.3	51.5 ± 1.5	
propanoic		4.72	−3418	28.4	54.5	−0.693	−1520	12.6	54.4	55.0 ± 2.0	
2-methylpropanoic	55.52 ± 0.28	6.71	−3660	30.4	56.1	1.60	−2470	20.5	56.3	53.0 ± 4.0	
butanoic	58.23 ± 0.30	7.52	−3970	33.0	58.1	2.83	−2970	24.7	58.5	58.0 ± 4.0	
2-methylbutanoic	61.98 ± 0.42	9.01	−4660	38.8		3.13	−3626	30.2			53.4 ± 3.0
3-methylbutanoic	61.24 ± 0.30	8.61	−4490	37.3		3.52	−3787	31.5			
pentanoic	63.04 ± 0.51	9.31	−4830	40.2		4.18	−4040	33.6			57.5 ± 3.0
2,2-dimethylpropanoic	59.71± 0.59[f]	7.71	−4090	34.0		3.51	−3240	26.9			62.4 ± 3.0[g]
3,3-dimethylbutanoic	63.97 ± 0.56	9.41	−4870	40.5		5.84	−4210	35.0			62.7 ± 3.0
hexanoic	69.19 ± 0.86	10.9	−5610	46.6						71.1 ± 1.3[h]	73.2 ± 2.0
heptanoic	72.93 ± 0.82	11.9	−6220	51.7						-	72.0 ± 1.5
octanoic	80.96 ± 0.62	13.0	−7529	62.6						80.3[i]	82.9 ± 1.0

[a] Derived from the transpiration in this work (see Table 1). [b] Calculated from correlation 5 (see text). [c] Calculated from correlation 6 (see text). [d] Taken from Konicek and Wadso (1970). [e] Taken from de Kruif and Oonk (1979). [f] Derived from the measured values $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\circ} = (62.09 \pm 0.55)$ kJ·mol^{-1} (Table 1) and $\Delta_{\rm cr}^{\rm l}H_{\rm m}^{\circ} = (2.38 \pm 0.21)$ kJ·mol^{-1} (measured by DSC). [g] Calculted using $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\circ} = (73.2 \pm 3.0)$ kJ·mol^{-1} (de Kruif and Oonk, 1979) with the help of $\Delta_{\rm cr}^{\rm l}H_{\rm m}^{\circ} = (2.38 \pm 0.21)$ kJ·mol^{-1} and $\Delta H_{\rm tr} = (8.11 \pm 0.21)$ kJ·mol^{-1} from this work. [h] Taken from Adriaanse et al. (1965). [i] Taken from Baccanar et al. (1968).

2. The values of $\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}$ for carboxylic acids were measured using two capillary columns of length 25 m and 50 m (Table 2). The technique applied correlates the values of $\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}$ of compounds whose $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ values are known with those of the compound of interest. We used our own experimental results for $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ from transpiration measurements (see Table 1) for the carboxylic acids C_5-C_8 in order to obtain the enthalpies of vaporization of the C_2-C_4 monocarboxylic acids. Correlation of the values of $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ of the carboxylic acids (Table 2) and the values of $\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}$ measured on the 25 m column gave the following equation:

$$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}/{\rm kJ\cdot mol^{-1}} = (32.70 \pm 0.20) + (0.772 \pm 0.020)\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}\ (r = 0.9940) \quad (5)$$

The correlation with the data $\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}$ measured on the column of 50 m length led to the equation

$$\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}/{\rm kJ\cdot mol^{-1}} = (44.2 \pm 0.11) + (0.568 \pm 0.014)\Delta_{\rm sol}^{\rm g}H_{\rm m}^{\circ}\ (r = 0.9981) \quad (6)$$

The comparison of the enthalpies of vaporization obtained by eqs 4 and 5 shows a very close agreement within the bounds of the experimental uncertainties of $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$, estimated to be about ±0.5 kJ·mol^{-1}.

Comparison of the $\Delta_l^g H_m^\circ$ Values Obtained by Transpiration and by Correlation Gas Chromatography, and Literature Values. Vapor−liquid equilibrium and vapor pressure measurements of monocarboxylic acids at higher temperatures have been studied as early as 1886. Obtaining the enthalpies of vaporization, measured ebulliometrically in the temperature ranges close to normal boiling points, and extrapolating them to the reference temperature leads to values with the drawbacks of accumulated uncertainties from experimental determination and ill-defined errors from extrapolation of $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ over the temperature range (100 to 150) K. These uncertainties will add up to (5 to 10) kJ·mol^{-1}. Moreover, obtaining reliable vaporization enthalpies, $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$, referred to the process RCOOH(liquid, 298.15 K) ⇔ RCOOH(gas, monomer, 298.15 K) for lower carboxylic acids from ebulliometric measurements is additionally exacerbated because of association in the vapor phase. The proper treatment of the $p-T$ data in this case to derive the enthalpy of vaporization requires knowledge of second virial coefficients, which are, as a rule, scarce. Hence, intercomparisons of our data with the ebulliometric results (Ambrose, 1981; Ambrose and Ghiassee, 1987) have not been made.

The enthalpies of vaporization of C_2-C_8 carboxylic acids available from the literature are given in Table 2. This table also presented the comparison of the values of $\Delta_{\rm l}^{\rm g}H_{\rm m}^{\circ}$ for the process RCOOH(liquid, 298.15 K) = RCOOH(gas, monomer, 298.15 K) obtained by transpiration and by correlation gas chromatography, and those known from the literature.

From the low-temperature vapor pressure measurements of the C_1-C_4 monocarboxylic acids using combined torsion- and weighting-effusion techniques (Calis-Van Ginkel et al., 1978) was found almost complete dimerization of the vapor phase (except in the case of butanoic acid). A substantial degree of dimerization of the vapor phase has been also observed for ethanoic and propanoic acids in our measurements of the vaporization enthalpies by means of the transpiration method (Verevkin et al., 2000).

As for the degree of dimerization α, the equilibrium constant of dimerization K is related to α by the equation (Prausnitz et al. 1986)

$$K = (\alpha/2)[1 - (\alpha/2)]/(1 - \alpha)^2 P \quad (7)$$

Equation 7 shows that, since K is a function only of temperature, α must go to zero as P approaches zero; in other words, dimerization decreases as the pressure falls. The surplus of the carrier gas in the transpiration experiment provides the reduction of the partial pressure of the carboxylic acid and decreases the degree of dimerization as a direct consequence of Le Chatelier's principle. It is not possible to assess the degree of dimerization of the vapor phase in the transpiration experiments quantitatively. But, the enthalpies of vaporization obtained from calorimetry (Konicek and Wadsö, 1970) and corrected to the process RCOOH(liquid, 298.15 K) ⇔ RCOOH(gas, monomer, 298.15 K) using data for dimerization enthalpies could be used as a criterion of the correctness of the enthalpies of vaporization measured by the transpiration method for lower carboxylic acids. Comparison of our results (Verevkin et al., 2000) at 298.15 K for the ethanoic [$\Delta_l^g H_m^\circ$ = (42.43 ± 0.83) kJ·mol^{-1}] and propanoic [$\Delta_l^g H_m^\circ$ = (51.40 ± 0.38) kJ·mol^{-1}] acids from transpiration shows the clear disagreement with those from Konicek and Wadsö (1970); see Table 2 (column 11). Following, the vapor phase contains associated molecules of acid in the transpiration experiments on both compounds. Obviously, the degree of dimerization decreases with the length of carbon chain attached to the carboxylic group. Let us compare the enthalpies of vaporization of C_4 carboxylic acids [2-methylpropanoic acid, $\Delta_l^g H_m^\circ$ = (55.52 ± 0.28) kJ·mol^{-1}; butanoic acid, $\Delta_l^g H_m^\circ$ = (58.23 ± 0.30) kJ·mol^{-1}] from transpiration techniques (Table 2, column 2) with those from Konicek and Wadsö (1970); see Table 2 (column 11). The results are in fair agreement, even taking into account the large error bars ascribed to the calorimetric measurements. Hence, we can draw the important conclusion from these experimental facts that for the C_4 carboxylic acids in the transpiration experiments the equilibrium of dimerization substantially shifted to the monomer form, or at least, it could be adopted that the content of associated molecules of acid in the vapor phase does not affect the correct determination of the vaporization enthalpy. Agreement of our results from the transpiration method for C_5-C_8 monocarboxylic acids (Table 2, column 2) with those from the literature (Table 2, column 12) measured using combined torsion- and weighting-effusion techniques (Calis-Van Ginkel et al., 1978) is also in good agreement within the error bars of (1 to 3) kJ·mol^{-1}. Following, the transpiration method could be successfully used for the determination of enthalpies of vaporization of the C_4-C_8 monocarboxylic acids without any corrections for the association of the vapor phase.

To support this conclusion, we decided to determine the enthalpies of vaporization of the C_4 monocarboxylic acids as well as ethanoic and propanoic acids by the correlation gas chromatography method. Since this method correlates the gas-chromatographical retention time of a compound of interest with the net of the retention times of some standard compounds with known enthalpies of vaporization, it has definitive advantages for application to carboxylic acids. First, the retention time of a carboxylic acid is a complex characteristic of its gas-chromatographical behavior, but this behavior is independent of the degree of association of an acid in the carrier gas in the GLC column. Second, a choice of standard compounds with known enthalpies of vaporization is arbitrary, but in the case of carboxylic acids it is reasonable to put into the correlation only C_5-C_8 monocarboxylic acids (Table 2, column 2), where the association of the vapor phase by using the transpiration technique could be neglected. Under such considerations, the desired enthalpies of vaporization of the C_2-C_4 monocarboxylic acids obtained from the correlation gas chromatography method should be definitely referred to the process RCOOH(liquid, 298.15 K) = RCOOH(gas, monomer, 298.15 K). The enthalpies of vaporization of the C_2-C_4 monocarboxylic acids were determined using two columns of different length (Table 2, columns 6 and 10). Results obtained on both columns are indistinguishable. At the same time these results are practically identical to those (Table 2, column 11) reported by Konicek and Wadsö (1970) and also to our own results (Table 2, column 2) for 2-methylpropanoic and butanoic acids from the transpiration method. Thus, we obtained consistent results for the enthalpies of vaporization of C_4 monocarboxylic acids from two different techniques. Our results for the enthalpies of vaporization of C_2-C_3 and C_5-C_8 monocarboxylic acids are consistent with those available from the literature, but the average accuracy of our data (less than 1 kJ·mol^{-1}) is substantially higher than that for the literature values (Table 2, columns 11 and 12). Due to this fact, we preferred our values for the further development of the method for the prediction of enthalpies of vaporization of monocarboxylic acids.

Table 3. Prediction of Enthalpies of Vaporization $\Delta_l^g H_m^\circ$ of the Monocarboxylic Acids at T = 298.15 K (in kJ·mol^{-1})

	$\Delta_l^g H_m^\circ$ [a]	$\Delta_l^g H_m^\circ$ [b]	Δ
acid	exp	calc	exp − calc
ethanoic acid	50.3 ± 0.5[c]	50.3	0.0
propanoic acid	54.4 ± 0.5[c]	53.4	1.0
2-methylpropanoic acid	55.52 ± 0.28	56.1	−0.6
butanoic acid	58.23 ± 0.30	58.4	−0.2
2-methylbutanoic acid	61.98 ± 0.42	61.1	0.9
3-methylbutanoic acid	61.24 ± 0.30	62.1	−0.9
pentanoic acid	63.04 ± 0.51	63.4	−0.4
2,2-dimethylpropanoic acid	59.71 ± 0.59	59.71	0.0
3,3-dimethylbutanoic acid	63.97 ± 0.56	64.7	−0.7
hexanoic acid	69.19 ± 0.86	68.4	0.8
heptanoic acid	72.93 ± 0.82	73.3	−0.4
octanoic acid	80.96 ± 0.62	78.3	2.7
2-ethylhexanoic acid	75.60 ± 0.42[d]	76.0	−0.4
nonanoic acid	82.42 ± 0.42[e]	83.3	−0.9
decanoic acid	89.4 ± 2.4[e,f]	88.3	1.1
tridecanoic acid	103.3 ± 2.7[e,f]	103.2	0.1
pentadecanoic acid	112.8 ± 4.6[e,f]	113.2	−0.4
nonadecanoic acid	131.1 ± 5.7[e,f]	133.1	−2.0

[a] From the transpiration method. [b] Calculated as the sum of increments (see text). [c] Calculated from correlation 6 (see text). [d] Taken from Stridh (1976). [e] Taken from Pilcher (1992). [f] Enthalpy of vaporization derived as $\Delta_l^g H_m^\circ = \Delta_{cr}^g H_m^\circ - \Delta_{cr}^l H_m^\circ$ taken from Pilcher (1992).

Prediction of the Enthalpies of Vaporization. This is not the fault of the empirical and half-empirical methods of estimation of the enthalpies of vaporization of organic compounds (Majer et al., 1989) but is due to ambiguous experimental data on monocarboxylic acids where only some coarse methods could be applied for the prediction of their enthalpies of vaporization (Majer et al., 1989). The enthalpies of vaporization of linear and branched carboxylic acids measured in this work together with the data for some higher monocarboxylic acids (Pilcher, 1992) provided the broad basis for the development of the precise and reliable methodology for the prediction of $\Delta_l^g H_m^\circ$. The summary of the data involved in the calculation is presented in Table 3. In recent years the group-additivity procedures have found a very successful application for the estimation of the thermodynamic properties. The molecular structure of the carboxylic acid could be represented as an increment for the COOH group and a sum of increments for the ajacent hydrocarbon chain. Group-additivity increments for hydrocarbons have been well defined (Majer et al., 1989): CH_3[C] = 5.65 kJ·mol^{-1}; CH_2[2C] = 4.98 kJ·mol^{-1}; CH[3C] = 3.01 kJ·mol^{-1}; C[4C] = 0.01 kJ·mol^{-1}. Because of the peculiarities of the carbon atoms attached directly to the carboxylic group, we suggested the following special increments for the estimation of the $\Delta_l^g H_m^\circ$ values of carboxylic acids: COOH[C] = (44.7 ± 1.1) kJ·mol^{-1}, CH_2[C, COOH] = (3.1 ± 1.2) kJ·mol^{-1}, CH[2C, COOH] = (0.1 ± 1.3) kJ·mol^{-1}, and C[3C, COOH] = −(1.9 ± 1.6) kJ·mol^{-1} have been estimated from the set of 18 experimental data points for acids (Table 3) handled by multilinear regression with the standard deviation from the correlation of 1.1 kJ·mol^{-1}.

Table 4. Prediction of Enthalpies of Formation $\Delta_f H^\circ_m$(g) of the Monocarboxylic Acids at $T = 298.15$ K (in kJ·mol^{-1})

	$\Delta^g_l H^\circ_m$ or		$\Delta_f H^\circ_m$(g)	$\Delta_f H^\circ_m$(g)		$\Delta_f H^\circ_m$(g)	$\Delta_f H^\circ_m$(g)
	$\Delta^g_{cr} H^\circ_m$ [a]	$\Delta_f H^\circ_m$(l or cr)[b]	exp	calc	Δ	MM3[c]	ab initio[d]
ethanoic(l)	50.3 ± 0.5	−484.3 ± 0.2	−434.1 ± 0.5	−434.1		−431.9	−433.0
propanoic(l)	54.4 ± 0.5	−510.7 ± 0.3	−456.3 ± 0.6	−453.2	−3.1	−452.2	−452.9
2-methylpropanoic(l)	55.52 ± 0.28	−532.1 ± 1.0[e]	−476.6 ± 1.0	−473.8	−2.8		
butanoic(l)	58.23 ± 0.30	−533.9 ± 0.6	−475.7 ± 1.1	−474.6	−1.1	−472.6	−472.7
2-methylbutanoic(l)	61.98 ± 0.42	−554.5 ± 5.9	−492.5 ± 5.9	−495.2	2.7		
3-methylbutanoic(l)	61.24 ± 0.30	−563.2 ± 1.0[e]	−502.0 ± 1.0	−501.3	−0.7	−502.3	
pentanoic(l)	63.04 ± 0.51	−559.4 ± 0.7	−496.4 ± 0.9	−496.1	−0.3	−493.2	−492.6
2,2-dimethylpropanoic(cr)	62.09± 0.55	−567.9 ± 1.1[e]	−505.8 ± 1.2	−505.8	0.0	−507.3	−513.4
3,3-dimethylbutanoic(l)	63.97 ± 0.56			−538.6			
hexanoic(l)	69.19 ± 0.86	−583.9 ± 1.6	−514.7 ± 1.8	−517.6	2.9	−513.7	−512.5
heptanoic(l)	72.93 ± 0.82	−610.2 ± 1.5	−537.3 ± 1.7	−539.0	1.7	−534.3	
octanoic(l)	80.96 ± 0.62	−636.0 ± 1.1	−555.0 ± 1.3	−556.2	1.2	−554.8	
2-ethylhexanoic(l)	75.60 ± 0.42	−635.1 ± 1.8	−559.5 ± 1.8	−559.6	0.1	−549.7	
nonanoic(l)	82.42 ± 0.42	−659.7 ± 2.0	−577.3 ± 2.1	−575.8	−1.5		
decanoic(cr)	118.9 ± 2.1[b]	−713.8 ± 1.0	−594.9 ± 2.3	−597.1	2.2		
tridecanoic (cr)	146.4 ± 2.1[b]	−806.6 ± 1.4	−660.2 ± 2.5	−658.8	−1.4		
pentadecanoic (cr)	162.8 ± 4.2[b]	−861.7 ± 1.6	−698.9 ± 4.5	−700.7	1.8		
nonadecanoic (cr)	198.7 ± 3.4[b]	−984.1 ± 2.4	−785.4 ± 5.6	−783.6	−1.8		

[a] From the transpiration metod; $\Delta^g_l H^\circ_m$ refers to the liquids, and $\Delta^g_{cr} H^\circ_m$ refers to the crystals. [b] Taken from Pilcher (1992). [c] Taken from Allinger et al. (1992a). [d] Taken from Allinger (1992b). [e] Taken from Ribeiro da Silva et al. (1999).

Prediction of the Enthalpies of Formation in the Gaseous State. The variety of carboxylic acids involved in organic synthesis is substantially broader than those investigated. Therefore, prediction of thermochemical properties is desirable. The enthalpies of formation in the condensed state of carboxylic acids C_1-C_{20} are well established by means of combustion calorimetry (Pilcher, 1992). With the new values of $\Delta^g_l H^\circ_m$ measured in this work we have established a more reliable basis for the calculation of the enthalpies of formation of carboxylic acids in the gaseous state. The scope of the data involved in the calculation is presented in Table 4. Similar to the case of our earlier work (Verevkin et al., 1996) we have introduced "strain-free" increments for the calculation of the $\Delta_f H^\circ_m$(g) values for the carboxylic acids. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H^\circ_m$(g) of simple homologous ("strainless") molecules. Strain-free group-additivity increments for hydrocarbons (Schleyer et al., 1970) are well defined. Their advantage with respect to the classic Benson increments (Benson, 1976) is the possibility to determine strain enthalpies. Generally, the molecular structure of the carboxylic acid could be described as an increment for the COOH group and a sum of increments for the ajacent hydrocarbon chain. The hydrocarbon increments (Schleyer et al., 1970) necessary in this work are as follows: $CH_3[C] = -42.05$ kJ·mol^{-1}; $CH_2[2C] = -21.46$ kJ·mol^{-1}; $CH[3C] = -9.04$ kJ·mol^{-1}; $C[4C] = -1.26$ kJ·mol^{-1}. We suggested the following increments for the estimation of the $\Delta_f H^\circ_m$(g) values of carboxylic acids: COOH[C], CH_2[C, COOH], CH[2C, COOH], and C[3C, COOH]. Using these group-additivity parameters and the values of $\Delta_f H^\circ_m$(g) for carboxylic acids (Table 4), the values of the strain-free increments COOH[C] = $-(392.1 \pm 2.0)$ kJ·mol^{-1}, CH_2[C, COOH] = $-(19.1 \pm 2.1)$ kJ·mol^{-1}, CH[2C, COOH] = (2.4 ± 2.4) kJ·mol^{-1}, and C[3C, COOH] = (12.4 ± 2.9) kJ·mol^{-1} have been estimated. We put into the correlation the set of 17 experimental data points for acids (Table 4) and handled them by multilinear regression with the standard deviation from the correlation of 2.0 kJ·mol^{-1}. To obtain strain-free increments, the data of strained molecules such as long chained carboxylic acids have to be corrected for strain (gauche-correction and 1,5 H-repulsions). The corrections for the strain enthalpies of 3-methylbutanoic acid (3.0 kJ·mol^{-1}), octanoic acid (4.3 kJ·mol^{-1}), nonanoic acid (6.1 kJ·mol^{-1}), decanoic acid (6.3 kJ·mol^{-1}), tridecanoic acid (9.0 kJ·mol^{-1}), pentadecanoic acid (10.0 kJ·mol^{-1}), and nonadecanoic acid (12.9 kJ·mol^{-1}) were estimated from the strains of the analogously branched hydrocarbons (Pedley et al., 1986) using the appropriate sum of the hydrocarbon increments as the strain-free reference. The mean values of the strain-free increments for carboxylic acids obtained in this work now are more reliable than before, because they are based on the experimental values of at least three enthalpies of formation for each parameter of the carboxylic acids except the increment C[3C, COOH].

The investigation of the 12 compounds in this work covered a broad range of structures of carboxylic acids. The measured enthalpies of vaporization and resulting standard enthalpies of formation fill the gap of available thermochemical data for acids and provide data to be used for the calculation of the thermochemical properties of compounds with similar structures. The recent development of the force field calculation methods (Allinger et al., 1992a) has already provided an accurate prediction of the enthalpies of formation of linear carboxylic acids (Table 4), but this method is still not adjusted for the branched representatives of this homological row. The extension in this work on an experimental basis to the thermochemistry of carboxylic acids could be helpful for the further parametrization of these force field methods. The ab initio calculation (Allinger et al., 1992b) is also able to reproduce the experimental enthalpies of formation of some "small" carboxylic acids generally within (1 to 3) kJ·mol^{-1} (see Table 4). The accurate calculation of larger molecules still remains a challenging task. Therefore, further development of the group-additivity methods remains important and increments derived in this work are useful for prediction of the thermochemical properties of carboxylic acids.

Literature Cited

Adriaanse, N.; Dekker, H.; Coops, J. Heats of combustion of normal saturated fatty acids and their methyl esters. *Rec. Trav. Chim. Pays/Bas* **1965**, *84*, 393−407.

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

Allinger, N. L.; Schmitz, L. R.; Motoc, I.; Bender, C.; Labanowski, J. Heats of formation of organic molecules by ab initio calculations: carboxylic acids and esters. *J. Comput. Chem.* **1992b**, *13*, 838−841.

Ambrose, D. Thermodynamic properties of organic oxygen compounds. LI. The vapour pressure of some esters and fatty acid. *J. Chem. Thermodyn.* **1981**, *13*, 795−802.

Ambrose, D.; Ghiassee, N. B. Vapour pressures and critical temperatures and critical pressures of some alkanoic acids: C_1 to C_{10}. *J. Chem. Thermodyn.* **1987**, *19*, 505−519.

Andereya, E.; Chase, J. D. The Implication of Carboxylic Acid Properties. *Chem. Eng. Technol.* **1990**, *13*, 304−312.

Baccanari, D. P.; Novinski, J. A.; Pan, Y.; Yevitz, M. M.; Swain, H. A., Jr. Heats of sublimation and vaporization at 25° of long chain fatty acids and methyl esters. *Trans. Faraday Soc.* **1968**, *64*, 1201−1205.

Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

Calis-Van Ginkel, C. H. D.; Calis, G. H. M.; Timmermans, C. W. M.; de Kruif, C. G.; Oonk, H. A. J. Enthalpies of sublimation and dimerization in the vapour phase of formic, acetic, propanoic, and butanoic acids. *J. Chem. Thermodyn.* **1978**, *10*, 1083−1088.

Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271−278.

Chickos, J. S.; Hesse, D. G.; Hosseini, S.; Liebman, J. F.; Mendenhall, G. D.; Verevkin, S. P.; Rakus, K.; Beckhaus, H.-D.; Rüchardt, C. Enthalpies of Vaporisation Some Highly Branched Hydrocarbons. *J. Chem. Thermodyn.* **1995**, *27*, 693- 705.

Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.

de Kruif, C. G.; Oonk, H. A. J. Enthalpies of vaporization and vapour pressures of seven aliphatic carboxylic acids. *J. Chem. Thermodyn.* **1979**, *11*, 287−290.

Jasperson, L. V.; Wilson, L. C.; Brady, C. J.; Wilding, W. V.; Wilson, G. M. Vapor association of monocarboxylic acids from heat vaporization and PVT measurements. *AICHE Symp. Ser.* **1989**, *85*, N271, 102−139.

Konicek, J.; Wadsö, I. Enthalpies of vaporization of organic compounds. VII. Some carboxylic acids. *Acta Chem. Scand.* **1970**, *24*, 2612−2626.

Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; IUPAC Chemistry Data Series 32; Blackwell Scientific Publications: London, 1985.

Majer, V.; Svoboda, V.; Pick, J. *Heats of Vaporization of Fluids*; Elsevier: Amsterdam, 1989.

Pedley, J. P.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

Pilcher, G. In *The Chemistry of Acid Derivatives*; Patai, S., Ed.; Wiley: New York, 1992; Vol. 2, Chapter 2.

Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice Hall Inc.: Englewood Cliffs, NJ, 1986; p 139.

Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Alves da Silva, A. M. R. O. Standard molar enthalpies of formation of three branched alkyl carboxylic acids. *J. Chem. Thermodyn.* **1999**, *31*, 1129−1134.

Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. B. The evaluation of strain in hydrocarbons. The strain in adamantane and its origin. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386.

Singh, N. B.; Glicksman, M. E. Physical properties of ultrapure pivalic acid. *Thermochim. Acta* **1990**, *159*, 93−99.

Stridh, G. Enthalpy of formation of 2-ethylhexanoic acid. *J. Chem. Thermodyn.* **1976**, *8*, 193−194.

Tsonopoulus, C.; Prausnitz, J. M. Fugacity Coefficients in Vapor-Phase Mixtures of Water and Carboxylic Acids. *Chem. Eng. J.* **1970**, *1*, 273−277.

Verevkin, S. P. Thermochemistry of Alcohols: Experimental Standard Molar Enthalpies of Formation and Strain of Some Alkyl and Phenyl Congested Alcohols. *Struct. Chem.* **1998**, *9*, 375−382.

Verevkin, S. P. Thermochemistry of Phenols. Quantification of the Ortho-, Para-, and Meta-interactions in Tert-alkyl Substituted Phenols. *J. Chem. Thermodyn.* **1999**, *31*, 559−585.

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.

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

Verevkin, S. P.; Bich, E.; Heintz, A. Determination of Vaporization Enthalpies of the Lower Carboxylic Acids from Transpiration Methods. *J. Chem. Eng. Data* **2000**, to be submitted.

Received for review October 18, 1999. Accepted March 29, 2000.

JE990282M