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Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for *trans*-Methyl Cinnamate, α-Methyl Cinnamaldehyde, Methyl Methacrylate, 1-Nonyne, Trimethylacetic Acid, Trimethylacetic Anhydride, and Ethyl Trimethyl Acetate

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The results of a study aimed at improvement of group-contribution methodology for estimation of thermodynamic properties of organic substances are reported. Specific weaknesses where particular group-contribution terms were unknown, or estimated because of lack of experimental data, are addressed by experimental studies of enthalpies of combustion in the condensed phase, vapor-pressure measurements, and differential scanning calorimetric heat-capacity measurements. Ideal-gas and condensed-phase enthalpies of formation of *trans*-methyl cinnamate, α-methyl cinnamaldehyde, methyl methacrylate, 1-nonyne, trimethylacetic acid, trimethylacetic anhydride, and ethyl trimethyl acetate are reported. Enthalpies of fusion were determined for *trans*-methyl cinnamate and trimethylacetic acid. Two-phase (solid + vapor) or (liquid + vapor) heat capacities were determined from 300 K to the critical region or earlier decomposition temperature for all the compounds. For ethyl trimethyl acetate, the values of the critical temperature and critical density were determined from the DSC results and the corresponding critical pressure was derived from the fitting procedures. The results of all the measurements were combined to derive a series of thermophysical properties including critical temperature, critical density, critical pressure, acentric factor, enthalpies of vaporization (restricted to within ±50 K of the temperature range of the vapor pressures), and heat capacities along the saturation line. Wagner-type vapor-pressure equations were derived for each compound. Group-additivity enthalpy of formation parameters and strain energies useful in the application of ideal-gas group-contribution correlations were derived.

Introduction

This research was funded jointly by the U.S. Department of Energy (DOE) through the Office of Fossil Energy within the Processing and Downstream Operations section of the Advanced Oil Recovery (AOR) program and the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. The objective of this ongoing project is to expand the group-additivity method of calculation of thermodynamic properties by determining thermochemical data on compounds containing unique groups or atomic environments. The work performed in the tenth year of this project (DIPPR Research Project 871: Determination of Pure Compound Ideal-Gas Enthalpies of Formation) represents the outcome of a meeting in late 1995, and subsequent communications, in which representatives of the DOE National Petroleum Technology Office, DIPPR, and BDM−Oklahoma at the National Institute for Petroleum and Energy Research (NIPER) agreed on a list of compounds for which the determination of the enthalpy of formation in the ideal-gas state would be of benefit to all the participants.

Seven compounds were chosen for experimental studies. The molecular structures, Chemical Abstracts Service (CAS) names, commonly used trivial names, and CAS Registry Numbers of the compounds studied are listed in Figure 1. Of the seven compounds studied, five were liquids at ambient temperature and the remaining two (*trans*-methyl cinnamate and trimethylacetic acid) were both crystalline solids. Hence, the derivation of ideal-gas standard enthalpies of formation for each of the compounds required experimental measurements in addition to the determination of the standard energies of combustion. A listing of the auxiliary measurements made for each of the compounds is given in Table 1.

The purity of the sample employed in a measurement of a thermodynamic property can significantly affect the accuracy of the measurement. The degree of inaccuracy introduced by the presence of impurities depends on a number of factors. In the case of the measurement of energies of combustion, with CO_2 analyses determining the amount of reaction, nonisomeric impurities are highlighted. The presence of a small amount of water (say 0.05 mol %) in the sample will often not be detected in the gas−liquid chromatographic analysis of the sample but is readily detected by the CO_2 analysis. Then, the determination of the energy of combustion should be based on the CO_2 analysis and not the mass of sample used in the calorimetric measurement. The presence of small amounts (less than 0.1%) of isomeric impurities usually will not have a significant effect on the result. However, this rule-of-thumb must be used with care, especially if the major impurity is an isomer with increased stability due to resonance or instability due to steric interactions. Measurements on

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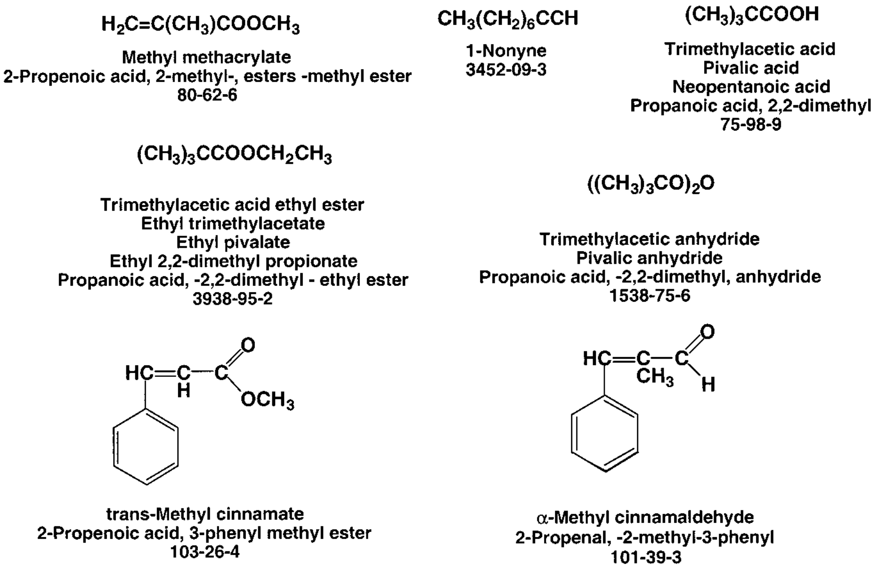

Figure 1. Structural formulas, common names, Chemical Abstracts Service names (provided by the authors), and Chemical Abstracts Service Registry Numbers (provided by the authors) for the compounds studied in this research.

Table 1. Outline of the Measurements Performed in This Project[a]

compd (state)	$\Delta_c U^\circ_m$	vapor pressure	heat capacity	T_c, ρ_c[b]
methyl methacrylate (l)	x	x		
trans-methyl cinnamate (cr)	x	x	x	
α-methyl cinnamaldehyde (l)	x	x	x	
1-nonyne (l)	x	x	x	
trimethylacetic acid (cr)	x	x	x	
trimethyl acetic anhydride (l)	x	x	x	
ethyl trimethyl acetate (l)	x	x	x	x

[a] Measurements made are donated by x. [b] From DSC measurements (a value for the critical pressure was derived using the fitting procedures). Values for the critical temperature, critical pressure, and critical density were derived using various procedures (see text) for each of the other six compounds.

samples whose purity is >99.95 mol % is a goal of this project.

There are in the literature numerous sets of Benson Group Parameters: Benson,[1] Benson et al.,[2] Cox and Pilcher,[3] Benson,[4] Reid et al.,[5] Cohen and Benson,[6] Domalski and Hearing,[7] and Cohen,[8] to name just a few. In addition, there are various other schemes that use extensions of the methodology: for example, Pedley et al.[9] and Pedley.[10] Also, in several papers, for example, Eigenmann et al.,[11] corrections to earlier work (in that case Benson[1]) were made. All these sets of parameters are different and cannot be interlaced. For example, the group $C-(C)_3(H)$ has a value of −7.95 kJ (−1.90 kcal) in ref 4. In ref 5, the corresponding value is also −7.95 kJ, but it is listed as −1.17 kJ in ref 7 and as −10.0 kJ in ref 8. To complicate the picture even more, it is believed that Reid et al.[5] used a value of 4.1868 and not 4.184 to convert from the thermochemical calorie used by Benson in his 1976 text[4] to the values reported in their text. By missing the Eigenmann et al. reference,[11] Reid et al.[5] did inadvertently use a mixture of corrected and outdated values for various oxygen-containing groups.

The differing sets of Benson Group Parameters need to be drawn together in one new comprehensive text. References 6 and 8 are partial attempts at that, but they are not nearly as comprehensive as the early work by Benson. Until someone or some group undertakes and completes the task, care should be taken in the selection of consistent sets of parameters. In the work reported on this project, care is taken to list *exactly* what group parameters are used in the additivity calculations; for example, the $C-(C)_3(H)$ group has a value of −7.95 kJ in all the calculations performed within the project. An attempt is made to use only Reid et al.[5] values, falling back on the Benson[4] tables if necessary and specially noting any and all exceptions. By doing this, reference is made to the most probable set of tables used by a practicing chemical engineer, and any errors in *that* text are highlighted.

Experimental Section

Since the combustion calorimetric techniques used differ from compound to compound, details of the combustion calorimetric methodology are given below. The apparatus and procedures used in obtaining the auxiliary experimental data (see Table 1) necessary to derive the ideal-gas enthalpies of formation have been previously described in the literature and in various DOE reports. In addition, the earlier papers published in this Journal under the DIPPR auspices[12−18] give detailed references to the experimental techniques and fitting procedures. Therefore, in this paper no details are given and the reader is referred to refs 12−18 and the earlier publications referenced therein.

Materials. To minimize errors due to impurities, care was taken to ensure only samples of high purity (>99.9 mol % purity) were subjected to the thermophysical property measurements. All compounds were purchased from Aldrich Chemical Co. Gas liquid chromatographic (GLC) analyses on the purchased samples gave an average purity of 98 mol %, in agreement with Aldrich specifications. The samples of α-methyl cinnamaldehyde, methyl methacrylate, 1-nonyne, trimethylacetic acid, trimethylacetic anhydride, and ethyl trimethyl acetate were all purified by repeated spinning-band distillations. *trans*-Methyl cinnamate was zone refined (100 passes). GLC analyses of the samples used in the measurements gave purities of at least 99.95 mol % for each compound. The high purity of each sample was confirmed subsequently by the percentage CO_2 recoveries in the combustion calorimetric measurements and/or by the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements listed in column 6 of Table 7.

A sample of the purified methyl methacrylate was transferred to the ebulliometer immediately after the final distillation. That sample was lost because of polymerization in the ebulliometer (see below). A second purified sample was used for the filling of the ampules for the combustion calorimetric study.

All transfers of the purified samples were done under nitrogen or helium or by vacuum distillation. The water used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The decane used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, decomposition of the complex with water, extraction with ether, drying with $MgSO_4$, and distillation at 337 K and 1 kPa pressure. GLC analysis of the decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1991 relative atomic masses[19] and the gas constant, $R = 8.314\,51$ $J\cdot K^{-1}\cdot mol^{-1}$, adopted by CODATA.[20] The platinum resistance thermometers and the quartz crystal thermometer used in these measurements were calibrated by comparison with standard platinum resistance thermometers whose constants were determined at the National Institute of Standards and Technology (NIST) on IPTS-68. All temperatures were measured in terms of IPTS-68 and converted to ITS-90 with increments provided in the literature.[21,22] Measurements of mass, time, electric resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

Energy of Combustion Apparatus and Procedures. The apparatus and experimental procedures used in the combustion calorimetry of organic C, H, O compounds at the National Institute for Petroleum and Energy Research have been described previously in refs 23−28.

A rotating-bomb calorimeter (laboratory designation BMR II)[29] and a platinum-lined bomb (laboratory designation Pt-3b)[30] with an internal volume of 0.3934 dm^3 were used without rotation in the combustion calorimetric series. Flexible borosilicate-glass ampules[24,31] were used to confine the samples which were liquid at 298 K (α-methyl cinnamaldehyde, methyl methacrylate, 1-nonyne, trimethylacetic anhydride, and ethyl trimethyl acetate). The sample of *trans*-methyl cinnamate was burned in pellet form. Trimethylacetic acid was also burned in pellet form but enclosed in a polyester-film bag.[29] All experiments, after the first, which defined the energy of combustion of the compound, were completed within 0.01 K of $T = 298.15$ K. For methyl methacrylate, the filled ampules were stored in the dark prior to use. In addition, the combustion of the filled ampules was accomplished in a 2 day interval without interruption by other combustion studies. A systematic change in the energy of combustion values would have been an indication of polymerization. No polymerization of the sample occurred during the combustion calorimetric study.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is −(26 434.0 ± 3.0) $J\cdot g^{-1}$ under certificate conditions. Conversion to standard states[32] gives −(26 413.7 ± 3.0) $J\cdot g^{-1}$ for $\Delta_c U^\circ_m/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in two separate series six-months apart, as the purified compounds became available. Except for the methyl methacrylate combustions (see above), calibration experiments were interspersed with each series of measurements. Nitrogen oxides were not formed in the calibration experiments or during the combustion calorimetry of any of the compounds because of the high purity of the oxygen used and preliminary bomb flushing. The energy equivalent of the calorimeter, ϵ(calor), obtained during each of the two calibration series was the same, namely (16 771.9 ± 0.5) $J\cdot K^{-1}$ (mean and standard deviation of eight measurements).

Table 2. Physical Properties at 298.15 K[a]

compd (state)	ρ $kg\cdot m^{-3}$	$10^7(\partial V/\partial T)_p$ $m^3\cdot K^{-1}\cdot mol^{-1}$	C_p/R
methyl methacrylate (l)	937	1.4	23.1[b]
trans-methyl cinnamate (cr)	1180	(0.3)	20.4
trans-methyl cinnamate (l)	1071[c]		
α-methyl cinnamaldehyde (l)	1039	1.6	31.0
1-nonyne (l)	754	1.8	32.1
trimethylacetic acid (cr)	980	(0.3)	23.1
trimethylacetic acid (l)	864[c]		
trimethylacetic anhydride (l)	918	1.5	41.0
ethyl trimethyl acetate (l)	856	1.5	29.9

[a] Values in parentheses are estimates. [b] Reference 35. [c] Measured for the liquid at 320 K.

Table 3. Carbon Dioxide Recoveries

compd	no. of expts	% recovery[a]
benzoic acid (calibration)	8	99.994 ± 0.004
trans-methyl cinnamate	8	99.957 ± 0.004
α-methyl cinnamaldehyde	9	99.957 ± 0.001
1-nonyne	10	99.989 ± 0.012
benzoic acid (calibration)	8	99.997 ± 0.003
methyl methacrylate	7	99.974 ± 0.003
trimethyl acetic acid	6	99.921 ± 0.006
trimethylacetic anhydride	6	99.987 ± 0.004
ethyl trimethyl acetate	7	99.916 ± 0.008

[a] Mean and standard deviation of the mean.

The auxiliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material, $\Delta_c U^\circ_m/M$ was −(46 042.5 ± 1.8) $J\cdot g^{-1}$ (mean and standard deviation). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^\circ_m/M$ was −16 945 $J\cdot g^{-1}$. The value for $\Delta_c U^\circ_m/M$ obtained for the polyester film, empirical formula $C_{10}H_8O_4$, was a function of the relative humidity (RH) in the laboratory during the weighing.[29]

$$\{(\Delta_c U^\circ_m/M)/(J\cdot g^{-1})\} = -22912.0 - 1.0560(RH) \qquad (1)$$

Information necessary for reducing the apparent mass measured in air to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states[32] is given in Table 2.

The values of density reported in Table 2 were measured in this laboratory, either from measurements of volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, for the liquid samples, or from the dimensions of a pellet of known mass for the compounds which were solid at 298.15 K (*trans*-methyl cinnamate and trimethylacetic acid). The values of the heat capacity of each sample [except methyl methacrylate (see below)] at 298.15 K were measured using a differential scanning calorimeter.

Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries.[25] The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. Summaries of the carbon dioxide recoveries for each of the two calibration series and the corresponding compound energy determinations are listed in Table 3. All the reported values for energies and enthalpies of combustion are based on the mass of CO_2 recovered and not the sample mass combusted.

Table 4. Typical Combustion Experiments at 298.15 K for Each of t Compounds ($p^\circ = 101.325$ kPa)[a,b]

	A	B	C	D
m'(compd)/g	0.970 631	1.073 098	0.829 606	0.674 263
m''(oil)/g	0.052 253		0.078 558	0.040 866
m'''(fuse)/g	0.002 781	0.002 258	0.002 470	0.002 373
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	39.282	19.367	38.665	39.163
ΔT^c/K	1.724 84	1.996 88	2.005 80	2.000 54
ϵ(calor)(ΔT)/J	−28 928.3	−33 490.1	−33 639.7	−33 552.9
ϵ(cont)(ΔT)^d/J	−37.5	−37.1	−43.8	−42.8
ΔU_{ign}/J	0.8	0.8	0.8	0.8
ΔU(corr.std.states)^e/J	15.2	21.3	18.1	10.7
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2405.9		3617.0	1881.6
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	47.1	38.1	41.8	40.2
$m'(\Delta_c U^\circ_m/M)$(compd)/J	−26 496.8	−33 467.0	−30 005.8	−31 662.4
$(\Delta_c U^\circ_m/M)$(compd)/J·g^{-1}	−27 298.7	−31 187.3	−36 168.7	−46 958.7

	E	F	G
m'(compd)/g	0.980 340	0.834 613	0.807 032
m''(oil)/g	0.0	0.065 301 8	0.054 08
m'''(mylar)/g	0.061 960	0.0	0.0
m''''(fuse)/g	0.002 668	0.002 569	0.002 801
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35
m(Pt)/g	39.282	38.457	38.665
ΔT^c/K	1.702 00	1.706 99	1.697 86
ϵ(calor)(ΔT)/J	−28545.4	−28 629.1	−28 476.3
ϵ(cont)(ΔT)^d/J	−35.6	−37.4	−36.6
ΔU_{ign}/J	0.8	0.8	0.8
ΔU(corr.std.states)^e/J	13.6	12.6	10.7
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	0.0	3006.6	2490.3
$-m'''(\Delta_c U^\circ_m/M)$(mylar)/J	1417.0	0.0	0.0
$-m''''(\Delta_c U^\circ_m/M)$(fuse)/J	45.2	43.5	39.7
$m'(\Delta_c U^\circ_m/M)$(compd)/J	−27 104.4	−25 603.0	−25 971.4
$(\Delta_c U^\circ_m/M)$(compd)/J·g^{-1}	−27 648.0	−30 676.5	−32 181.4

[a] **A** = methyl methacrylate; **B** = *trans*-methyl cinnamate; **C** = α-methyl cinnamaldehyde; **D** = 1-nonyne; **E** = trimethylacetic acid; **F** = trimethylacetic anhydride; and **G** = ethyl trimethyl acetate. [b] The symbols and abbreviations of this table are those of ref 27 except as noted. [c] $\Delta T/K = (T_i - T_f + \Delta T_{corr})/K$. [d] $\epsilon_i(cont)(T_i - 298.15\ K) + \epsilon_f(cont)(298.15\ K - T_f + \Delta T_{corr})$. [e] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of ref 27.

Results

Combustion Calorimetry. A typical combustion experiment for each C, H, O compound studied is summarized in Table 4. It is impractical to list summaries for each combustion; $\Delta_c U^\circ_m/M$ values for all the combustion calorimetric measurements made on each of these compounds are reported in Table 5. The values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for the C, H, O compounds refer to the general reaction

$$C_aH_bO_c(\text{cr or l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) \quad (2)$$

As noted above, all the values of $\Delta_c U^\circ_m/M$ refer to the unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products.

Table 6 gives derived values of the standard molar energy of combustion $\Delta_c U^\circ_m$; the standard molar enthalpy of combustion $\Delta_c H^\circ_m$; and the standard molar enthalpy of formation $\Delta_f H^\circ_m$ for the compounds studied. Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ for the C, H, O compounds refer to eq 2. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$aC(\text{cr, graphite}) + \frac{b}{2}H_2(g) + \frac{c}{2}O_2(g) = C_aH_bO_c(\text{cr or l}) \quad (3)$$

The uncertainties given in Table 6 are the "uncertainty interval."[33] The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be $-(393.51 \pm 0.13)$ kJ·mol^{-1} and $-(285.830 \pm 0.042)$ kJ·mol^{-1}, respectively, as assigned by CODATA.[34]

Vapor-Pressure Measurements. Ebulliometric vapor-pressure measurements were made on each of the seven compounds of this study. Results of the measurements are reported in Table 7. In the table, the vapor pressure, the condensation temperature, and the difference between the condensation and boiling temperatures are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied.

The difference between the boiling and condensation temperatures (ΔT) for methyl methacrylate increased significantly above 373 K (see Table 7). An attempt was made to make a measurement at 169 kPa (403 K), but the sample formed a glass in the ebulliometer. Removal of the polymeric material subsequently formed was difficult and eventually involved flaming with a glassblowing torch in an oxygen flow. For the *trans*-methyl cinnamate sample above 560 K, decomposition was indicated by a slow increase in ΔT. For the α-methyl cinnamaldehyde, sample decomposition became extensive above 560 K.

Differential Scanning Calorimetry. Table 8 lists equations representing the variation of saturated heat capacity $C_{sat,m}$ with temperature for each of the compounds studied. The derived equations were determined from DSC measurements for various cell fillings. Heat capacities were determined at 20 K intervals with a heating rate of 0.083 K·s^{-1} and a 120 s equilibration period between energy additions. For each compound the upper temperature bound of the measurements was set by the critical region (ethyl trimethyl acetate) or earlier sample decomposition.

There exists in the literature values of the heat capacity and derived thermodynamic functions for both methyl methacrylate and its homopolymer.[35] Because of that presence and the difficulty in keeping samples of the monomer for any period of time (see above), no detailed heat-capacity measurements were performed in this research. For each of the other compounds studied, except ethyl trimethyl acetate, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. For ethyl trimethyl acetate measurements in the critical region were possible. For that compound, an abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed. Sample decomposition was greatly reduced by employing a single continuous heat at a heating rate of 0.333 K·s^{-1}. Temperatures at which conversion to the single phase occurred were measured for several cell fillings. Table 9 reports the density, obtained from the mass of sample and the cell volume, V_x, calculated with eq 4

$$V_x(T)/V_x(298.15\text{ K}) = 1 + ay + by^2 \quad (4)$$

where $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}$ K^{-1}, and $b = 5.4 \times 10^{-8}$ K^{-2}, and the measured temperatures at which conversion to a single phase were observed.

A critical temperature $T_c = (566 \pm 1)$ K and a corresponding critical density $\rho_c = (280 \pm 10)$ kg·m^{-3} were derived graphically for ethyl trimethyl acetate from these results, as seen in Figure 2. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported.[36] The rapid heating method was used previously for critical

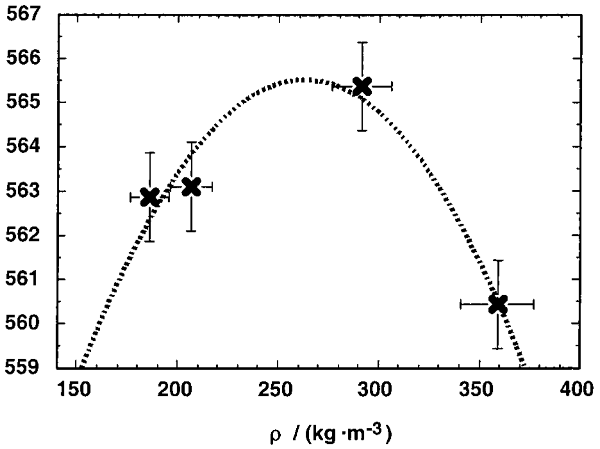

Figure 2. Vapor–liquid coexistence in the region of the critical point for ethyl trimethyl acetate. The curve is drawn as an aid to the eye and does not represent any theoretically valid equation. The crosses span the range of uncertainty.

temperature and critical density determinations for 2-aminobiphenyl,[37] dibenzothiophene,[38] and carbazole and benzofuran.[39]

For *trans*-methyl cinnamate and trimethylacetic acid, which were solids at ambient temperature, by judicious choice of starting temperature, the melting endotherm during the DSC enthalpy measurements occurred in the center of a heating cycle. The measured enthalpies during those particular heating cycles contained the enthalpy of fusion plus enthalpies for raising the solid from the initial temperature to the melting point and for raising the liquid from the melting point to the final temperature. The derived enthalpies of fusion for *trans*-methyl cinnamate and trimethylacetic acid at their respective melting points and at 298.15 K are reported in Table 8. Equations, representing the heat capacities for the liquid and solid phases, which were used in the "adjustment" to 298.15 K, are also reported in Table 8. (Note: all the heat-capacity equations should only be used to derive values within the temperature ranges specified in Table 8; extrapolation outside the temperature range will produce erroneous values.)

Fitting Procedures. The main goal of the fitting procedures was to derive accurate enthalpies of vaporization for each compound over as wide a temperature range as possible. Although $\Delta_l^g H_m$ at 298.15 K is the only value necessary to obtain $\Delta_f H_m^\circ$(g, 298.15 K), the benefit of knowledge of the enthalpy of vaporization over a wide range of temperature was recognized. The exact fitting procedure used for each compound varies depending on the range of measured properties (vapor pressures and heat capacities) available.[39]

The fitting parameters were derived by a nonlinear least-squares fit of the vapor pressures listed in Table 7 using the Wagner equation[40] in the formulation given by Ambrose and Walton:[41]

$$\ln(p/p_c) = (1/T_r)[AY + BY^{1.5} + CY^{2.5} + DY^5] \qquad (5)$$

where $T_r = T/T_c$ and $Y = (1 - T_r)$. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in ref 39. The number of fitting parameters differed depending on whether a critical temperature could be determined experimentally. For ethyl trimethyl acetate, a critical temperature was determined from the DSC measurements and, hence, only the critical pressure p_c was included in the variables. For the remaining compounds, estimates were made for the critical temperature using literature techniques such as those due to Joback[42] and Ambrose[43] to guide the selection of values.

For ethyl trimethyl acetate, a simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 7 and the two-phase heat capacities $C_{x,m}^{II}$ given in Table 8B was completed. The fitting procedure has been described in detail in ref 39, and hence, only a summary of the procedure follows. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in ref 39. For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C_{x,m}^{II}$ values (Table 2) were converted to $C_{V,m}^{II}$

Table 5. Energy of Combustion Results (T = 298.15 K and p° = 101.325 kPa)[a,b]

compd	$\{(\Delta_c U_m^\circ/M)(\text{compd})\}/(\text{J·g}^{-1})$	$\langle\{(\Delta_c U_m^\circ/M)(\text{compd})\}/(\text{J·g}^{-1})\rangle$
methyl methacrylate	−27 298.7, −27 306.2, −27 301.7, −27 305.4, −27 299.4, −27 298.7, −27 297.6	−27 301.1 ± 1.3
trans-methyl cinnamate	−31 187.3, −31 187.5, −31 186.3, −31 186.2, −31 188.3, −31 187.7, −31 189.5, −31 190.0	−31 187.9 ± 0.5
α-methyl cinnamaldehyde	−36 168.7, −36 157.5, −36 171.0, −36 152.7, −36 155.5, −36 156.3, −36 178.9, −36 159.8, −36 155.0	−36 159.5 ± 2.1
1-nonyne	−46 960.0, −46 970.8, −46 956.3, −46 971.0, −46 960.4, −46 967.2, −46 959.3, −46 958.7, −46 958.4, −46 960.7	−46 962.3 ± 1.7
trimethylacetic acid	−27 648.0, −27 649.5, −27 655.8, −27 654.7, −27 645.0, −27 651.3	−27 650.7 ± 1.7
trimethylacetic anhydride	−30 676.5, −30 681.2, −30 680.8, −30 681.4, −30 675.2, −30 677.0	−30 678.7 ± 1.1
ethyl trimethyl acetate	−32 181.4, −32 182.5, −32 176.0, −32 180.9, −32 169.5, −32 179.4, −32 175.4	−32 177.9 ± 1.7

[a] The uncertainties shown are one standard deviation of the mean. [b] All the energy of combustion measurements made for each compound are listed in this table.

Table 6. Condensed-Phase Molar Thermochemical Functions at 298.15 K and p° = 101.325 kPa[a]

	$\Delta_c U_m^\circ$/kJ·mol^{-1}	$\Delta_c H_m^\circ$/kJ·mol^{-1}	$\Delta_f H_m^\circ$/kJ·mol^{-1}
methyl methacrylate (l)	−2733.33 ± 0.46	−2735.80 ± 0.46	−375.07 ± 0.54
trans-methyl cinnamate (cr)	−5058.32 ± 0.76	−5062.04 ± 0.76	−302.21 ± 0.88
α-methyl cinnamaldehyde (l)	−5286.14 ± 0.96	−5291.09 ± 0.96	−73.16 ± 1.08
1-nonyne (l)	−5833.98 ± 0.88	−5843.90 ± 0.88	15.67 ± 1.02
trimethylacetic acid (cr)	−2824.07 ± 0.52	−2827.79 ± 0.52	−568.91 ± 0.60
trimethylacetic anhydride (l)	−5713.97 ± 0.90	−5721.41 ± 0.90	−786.16 ± 1.06
ethyl trimethyl acetate (l)	−4189.16 ± 0.70	−4195.36 ± 0.70	−560.02 ± 0.82

[a] The results listed in this table are for the stable [liquid (l) or crystalline (cr)] condensed phase at 298.15 K for each of the compounds.

Table 7. Summary of Vapor-Pressure Results[a]

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
Methyl Methacrylate											
decane	294.785	4.0016	0.0014	0.0006	0.017	water	345.100	38.577	−0.006	0.004	0.025
decane	300.183	5.3296	−0.0014	0.0007	0.017	water	350.737	47.374	−0.011	0.005	0.028
decane	308.251	8.0057	−0.0029	0.0010	0.017	water	356.410	57.797	−0.011	0.006	0.028
decane	314.255	10.668	0.000	0.001	0.020	water	362.141	70.116	−0.006	0.007	0.027
decane	319.107	13.323	0.000	0.002	0.021	water	367.893	84.510	0.020	0.008	0.029
decane	324.191	16.673	0.000	0.002	0.020	water	373.686[b]	101.293	0.076	0.010	0.032
decane	328.345	19.907	0.005	0.002	0.024	water	379.517[b]	120.76	0.19	0.01	0.042
decane	333.913	25.027	0.004	0.003	0.023	water	385.389[b]	143.19	0.33	0.01	0.038
water	339.496	31.196	0.002	0.004	0.028						
trans-Methyl Cinnamate											
decane	409.272	2.0094	−0.0002	0.0003	0.088	water	494.647	38.553	0.004	0.004	0.046
decane	425.751	3.9927	0.0012	0.0005	0.050	water	502.366	47.396	0.002	0.005	0.050
decane	433.184	5.3254	−0.0004	0.0006	0.042	water	510.078	57.810	−0.002	0.005	0.054
decane	444.199	7.9869	−0.0005	0.0009	0.034	water	517.853	70.112	−0.004	0.006	0.061
decane	452.456	10.6500	−0.0007	0.0011	0.030	water	525.655	84.498	−0.004	0.007	0.069
decane	459.144	13.320	0.000	0.001	0.029	water	533.516	101.296	−0.004	0.009	0.078
decane	466.088	16.660	−0.001	0.002	0.028	water	541.418	120.78	0.01	0.01	0.095
decane	471.829	19.923	0.000	0.002	0.032	water	549.336[b]	143.19	0.02	0.01	0.113
decane	479.397	25.013	−0.001	0.002	0.032	water	557.294[b]	168.95	0.08	0.01	0.143
water	487.014	31.181	0.005	0.003	0.043						
α-Methyl Cinnamaldehyde											
decane	401.503	2.0058	−0.0001	0.0003	0.110	water	486.145	38.574	0.006	0.004	0.022
decane	417.894	4.0004	−0.0002	0.0005	0.048	water	493.757	47.359	0.001	0.005	0.021
decane	425.207	5.3286	0.0009	0.0006	0.046	water	501.456	57.832	0.000	0.005	0.024
decane	436.141	7.9999	0.0000	0.0009	0.036	water	509.158	70.109	0.001	0.006	0.026
decane	444.314	10.6646	−0.0004	0.0011	0.031	water	516.917	84.519	−0.013	0.007	0.027
decane	450.915	13.325	−0.001	0.001	0.029	water	524.721	101.322	0.009	0.009	0.033
decane	457.806	16.670	−0.001	0.002	0.024	water	532.552	120.77	0.00	0.01	0.032
decane	463.504	19.937	−0.001	0.002	0.024	water	540.417	143.20	−0.01	0.01	0.038
decane	470.987	25.014	0.000	0.002	0.022	water	548.327	169.00	0.01	0.01	0.052
water	478.545	31.176	0.003	0.003	0.020	water	556.237[b]	198.36	0.05	0.01	0.074
1-Nonyne											
decane	320.529	2.0007	−0.0001	0.0003	0.024	water	397.691	47.364	0.000	0.005	0.003
decane	334.143	3.9982	0.0006	0.0005	0.013	water	404.181	57.799	0.000	0.006	0.003
decane	340.277	5.3390	−0.0002	0.0007	0.010	water	410.721	70.093	0.000	0.007	0.003
decane	349.316	7.9922	−0.0002	0.0010	0.008	water	417.305	84.484	0.001	0.008	0.002
decane	356.152	10.6615	−0.0007	0.0012	0.006	water	423.955	101.292	−0.002	0.009	0.002
decane	361.661	13.317	−0.001	0.002	0.005	water	430.642	120.75	0.00	0.01	0.003
decane	367.408	16.648	0.000	0.002	0.005	water	437.380	143.19	0.00	0.01	0.002
decane	372.191	19.917	0.001	0.002	0.004	water	444.167	168.96	0.00	0.01	0.002
decane	378.513	25.024	0.001	0.002	0.003	water	451.006	198.44	0.00	0.02	0.003
water	384.859	31.176	0.000	0.003	0.003	water	457.891	231.98	0.00	0.02	0.003
water	391.248	38.556	0.000	0.004	0.003	water	464.814	269.95	0.00	0.02	0.004
Trimethylacetic Acid											
decane	343.992	1.9987	0.0004	0.0003	0.038	water	414.363	47.361	0.000	0.005	0.007
decane	356.777	3.9951	−0.0006	0.0006	0.030	water	420.080	57.797	−0.002	0.006	0.006
decane	362.440	5.3259	−0.0010	0.0007	0.021	water	425.827	70.119	−0.006	0.007	0.006
decane	370.854	8.0020	−0.0009	0.0010	0.017	water	431.577	84.529	−0.002	0.008	0.007
decane	377.096	10.6662	0.0001	0.0013	0.016	water	437.343	101.300	−0.008	0.010	0.005
decane	382.129	13.331	0.000	0.002	0.014	water	443.129	120.75	−0.01	0.01	0.007
decane	387.341	16.666	0.001	0.002	0.013	water	448.940	143.19	−0.02	0.01	0.005
decane	391.639	19.924	0.003	0.002	0.013	water	454.763	168.97	0.01	0.01	0.008
decane	397.334	25.050	0.003	0.003	0.011	water	460.615	198.44	0.02	0.02	0.009
water	402.980	31.175	0.001	0.004	0.009	water	466.476[b]	231.94	0.05	0.02	0.011
water	408.670	38.568	0.002	0.004	0.008	water	472.369[b]	269.96	0.08	0.02	0.012
Trimethylacetic Anhydride											
decane	355.222	2.0024	0.0001	0.0003	0.052	water	439.727	47.353	0.002	0.005	0.013
decane	370.107	3.9951	−0.0005	0.0005	0.037	water	446.857	57.819	0.005	0.006	0.014
decane	376.794	5.3296	0.0001	0.0006	0.030	water	454.043	70.142	−0.006	0.007	0.011
decane	386.738	7.9940	0.0016	0.0009	0.027	water	461.237	84.496	−0.005	0.008	0.011
decane	394.232	10.6632	−0.0011	0.0012	0.019	water	468.529	101.322	−0.002	0.009	0.012
decane	400.275	13.324	−0.001	0.001	0.018	water	475.852	120.77	0.00	0.01	0.012
decane	406.581	16.662	−0.001	0.002	0.016	water	483.226	143.18	0.00	0.01	0.011
decane	411.806	19.922	0.000	0.002	0.016	water	490.674	168.99	0.00	0.01	0.011
decane	418.718	25.021	0.001	0.002	0.016	water	498.164	198.44	0.00	0.02	0.014
water	425.675	31.175	−0.001	0.003	0.013	water	505.710	231.97	−0.01	0.02	0.014
water	432.673	38.554	0.001	0.004	0.015	water	513.294	269.95	0.00	0.02	0.017

Table 7. (Continued)

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
						Ethyl Trimethyl Acetate					
decane	307.799	3.9882	0.0006	0.0006	0.019	water	373.004	57.801	−0.003	0.006	0.007
decane	313.542	5.3364	−0.0011	0.0007	0.015	water	379.102	70.102	−0.003	0.007	0.007
decane	321.979	8.0028	−0.0005	0.0010	0.014	water	385.239	84.492	−0.001	0.008	0.008
decane	328.318	10.6688	0.0004	0.0013	0.013	water	391.438	101.293	−0.001	0.009	0.008
decane	333.452	13.332	0.000	0.002	0.011	water	397.680	120.75	0.00	0.01	0.008
decane	338.781	16.656	0.001	0.002	0.012	water	403.970	143.20	0.00	0.01	0.009
decane	343.219	19.916	0.001	0.002	0.010	water	410.308	168.97	0.01	0.01	0.008
decane	349.107	25.030	0.001	0.003	0.009	water	416.692	198.42	0.01	0.02	0.008
water	355.004	31.171	−0.002	0.004	0.008	water	423.129	231.96	0.00	0.02	0.007
water	360.965	38.568	−0.001	0.004	0.008	water	429.606	269.94	−0.01	0.02	0.007
water	366.960	47.372	0.001	0.005	0.008						

[a] Water (w) or decane (d) refers to which material was used as the standard in the reference ebulliometer. T is the condensation temperature of the sample; the pressure p was calculated from the condensation temperature of the reference substance; and Δp is the difference of the value of pressure, calculated with eq 5 and the parameters listed in Table 10, from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$). σ is the propagated error calculated using $\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$. ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Values at this temperature were not included in the fit of the Wagner equation because of sample decomposition, which was indicated by the increase in ΔT values or, in the case of methyl methacrylate, by polymer formation (see text).

Table 8. Heat Capacity Equations and Enthalpies of Fusion and Two-Phase (Liquid + Vapor) Heat Capacities Derived from DSC Measurements (R = 8.314 51 J·K^{-1}·mol^{-1})

A. Heat Capacity Equations and Enthalpies of Fusion

trans-Methyl Cinnamate (crystalline)
$C_{\mathrm{sat,m}}/R = 0.04T + 8.5$ (in temperature range 290 K to 309 K)

trans-Methyl Cinnamate (liquid)
$C_{\mathrm{sat,m}}/R = 0.053T + 16.8$ (in temperature range 309 K to 550 K)
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$(*trans*-methyl cinnamate, 309 K) = 33.1 ± 0.8 kJ·mol^{-1}
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$(*trans*-methyl cinnamate, 298.15 K) = 32.0 ± 1.0 kJ·mol^{-1}

α-Methyl Cinnamaldehyde (liquid)
$C_{\mathrm{sat,m}}/R = 0.0515T + 15.6$ (in temperature range 290 K to 470 K)

1-Nonyne (liquid)
$C_{\mathrm{sat,m}}/R = 0.06T + 14.2$ (in temperature range 290 K to 450 K)

Trimethylacetic Acid (crystalline)
$C_{\mathrm{sat,m}}/R = 0.055T + 6.7$ (in temperature range 290 K to 309.1 K)

Trimethylacetic Acid (liquid)
$C_{\mathrm{sat,m}}/R = 0.078T + 0.26$ (in temperature range 309.1 K to 440 K)
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$(trimethylacetic acid, 309.1 K) = 2.3 ± 0.2 kJ·mol^{-1}
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$(trimethylacetic acid, 298.15 K) = 2.4 ± 0.3 kJ·mol^{-1}

Trimethylacetic Anhydride (liquid)
$C_{\mathrm{sat,m}}/R = 0.069T + 20.4$ (in temperature range 290 K to 450 K)

B. Two-Phase (Liquid + Vapor) Heat Capacities for Ethyl Trimethyl Acetate

	$C_{\mathrm{X,m}}^{\mathrm{II}}/R$		
T/K	m/g = 0.010 890 $V_c{}^a$ = 0.0528	m/g = 0.015 391 $V_c{}^a$ = 0.0528	m/g = 0.018 580 $V_c{}^a$ = 0.0528
308.15	30.4	31.1	30.6
328.15	31.6	32.3	31.7
348.15	32.6	33.4	32.9
368.15	33.7	34.4	33.9
388.15	35.2	35.6	35.0
408.15	37.0	37.1	36.3
428.15	38.8	38.0	37.6
448.15	40.7	39.4	38.9
468.15	42.7	40.5	40.3
488.15	44.9	42.5	41.1
508.15	47.4	43.9	42.4
528.15	55.9	46.7	44.3
548.15	59.6	51.6	50.2
568.15[b]	36	34	45

[a] Volume of cell in cubic centimeters is given at 298.15 K. [b] Values not included in fit. Values are listed to show the large drop in heat capacity on passing into the fluid phase.

by means of eq 4 for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{\mathrm{sat}}$,

$$C_{V,\mathrm{m}}^{\mathrm{II}} = C_{x,\mathrm{m}}^{\mathrm{II}} - T/n\{(\partial V_x/\partial T)_x(\partial p/\partial T)_{\mathrm{sat}}\} \tag{6}$$

The values of $C_{V,\mathrm{m}}^{\mathrm{II}}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{\mathrm{sat}}$ and $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ (see eq 2 of ref 39). The functional form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2\mu/\partial T^2)_{\mathrm{sat}}/(\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}}) = \sum_{i=0}^{3} b_i(1 - T/T_{\mathrm{c}})^i \tag{7}$$

Details of the weighting procedures and so forth are given by Steele.[39]

The remaining six compounds decomposed well removed from the critical region, and the measured $C_{x,\mathrm{m}}^{\mathrm{II}}$ values were virtually independent of cell filling. Hence, fitting procedures were restricted to include the Wagner vapor-pressure equation only. Corresponding critical pressures were selected with Waring's criterion for $T_{\mathrm{r}} = 0.85$.[44] Application of this criterion was discussed recently by Steele.[39] Table 10 listed the parameters derived using the procedures outlined above. Details of the fits using the vapor-pressure results are given in Table 7 (column 4, labeled $\Delta p = p - p_{\mathrm{Wagner}}$, with p_{Wagner} calculated using the parameters listed in Table 10).

Values of $C_{V,\mathrm{m}}^{\mathrm{II}}(\rho{=}\rho_{\mathrm{sat}})$ were derived for ethyl trimethyl acetate from the parameters listed in Table 10, and corresponding $C_{\mathrm{sat,m}}$ values were obtained using eq 6 of ref 39. The results for $C_{\mathrm{sat,m}}/R$ are reported in Table 11. The estimated uncertainty in these values is 1%.

Enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (Table 12) were derived from the Wagner-equation fits using the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}/(T\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}) \tag{8}$$

where $\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}$ is the increase in molar volume from the liquid to the real vapor. Estimates of the liquid-phase molar volumes, $V_{\mathrm{m}}(\mathrm{l})$, were made with the extended corresponding-states equation of Riedel[45] as formulated by Hales and Townsend:[46]

$$\rho/\rho_{\mathrm{c}} = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \tag{9}$$

with $Y = (1 - T/T_{\mathrm{c}})$, ρ_{c} = critical density, and ω = acentric factor. The acentric factor, ω, is defined as $[-\log(p/p_{\mathrm{c}}) - 1]$, where p is the vapor pressure at $T/T_{\mathrm{c}} = 0.7$ and p_{c} is

Table 9. Densities and Temperatures Used To Define the Two-Phase Dome near T_c

ρ/kg·m^{-3}	T/K
Ethyl Trimethyl Acetate	
185.9	562.9
206.1	563.1
291.4	565.4
358.9	560.4

Table 10. Parameters for the Wagner Equation (Eq 5) and Eq 7, and Critical Constants and Acentric Factors[a]

Methyl Methacrylate				*trans*-Methyl Cinnamate			
A	−7.572 93			A	−9.843 65		
B	2.514 45			B	4.681 66		
C	−4.946 24			C	−5.880 13		
D	−0.650 48			D	−3.236 40		
T_c	563 K	p_c	3670 kPa	T_c	T_c762 K	p_c	3500 kPa
ρ_c	318 kg·m^{-3}	ω	0.3054	ρ_c	ρ_c320 kg·m^{-3}	ω	0.5396
α-Methyl Cinnamaldehyde				1-Nonyne			
A	−12.545 43			A	−8.403 34		
B	10.121 54			B	2.709 82		
C	−9.064 54			C	−3.908 14		
D	−1.969 69			D	−4.231 90		
T_c	764 K	p_c	4850 kPa	T_c	611 K	p_c	2900 kPa
ρ_c	302 kg·m^{-3}	ω	0.5824	ρ_c	242 kg·m^{-3}	ω	0.4137
Trimethylacetic Acid				Trimethylacetic Anhydride			
A	−9.608 52			A	−8.643 72		
B	3.948 31			B	2.360 06		
C	−7.506 10			C	−4.373 03		
D	−1.318 98			D	−4.596 25		
T_c	633 K	p_c	5000 kPa	T_c	642 K	p_c	2000 kPa
ρ_c	267 kg·m^{-3}	ω	0.6174	ρ_c	281 kg·m^{-3}	ω	0.5089
Ethyl Trimethyl Acetate							
A	−8.849 72	b_0	−0.605 13				
B	3.895 63	b_1	−0.102 29				
C	−4.937 91	b_2	−1.172 52				
D	−3.126 72	b_3	0.785 49				
T_c	566 K	p_c	2950 kPa				
ρ_c	280 kg·m^{-3}8	ω	0.405				

[a] The parameters listed in this table are those derived from the various procedures described in the text.

Table 11. Values of $C_{\mathrm{sat,m}}/R$ for Ethyl Trimethyl Acetate (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{\mathrm{sat,m}}/R$	T/K	$C_{\mathrm{sat,m}}/R$
300	30.0	440	37.2
320	31.1	460	38.4
340	32.2	480	39.9
360	33.2	500	41.8
380	34.2	520	44.6
400	35.1	540	49.7
420	36.1		

Table 12. Enthalpies of Vaporization Obtained from the Wagner and Clapeyron Equations[a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
Methyl Methacrylate			
280.0[b]	39.93 ± 0.13	360.0	34.90 ± 0.23
298.15	38.92 ± 0.13	380.0	33.34 ± 0.35
300.0	38.81 ± 0.13	400.0[b]	31.63 ± 0.48
320.0	37.62 ± 0.13	420.0[b]	29.77 ± 0.63
340.0	36.33 ± 0.17	440.0[b]	27.76 ± 0.81
trans-Methyl Cinnamate			
298.15[b,c]	69.99 ± 0.43	480.0	55.32 ± 0.25
360.0[b]	64.69 ± 0.27	500.0	53.75 ± 0.32
380.0[b]	63.07 ± 0.25	520.0	52.14 ± 0.40
400.0[b]	61.48 ± 0.23	540.0	50.48 ± 0.52
420.0	59.92 ± 0.22	560.0	48.73 ± 0.67
440.0	58.39 ± 0.22	580.0[b]	46.91 ± 0.85
460.0	56.86 ± 0.22	600.0[b]	45.0 ± 1.1
α-Methyl Cinnamaldehyde			
298.15[b]	67.52 ± 0.35	480.0	53.39 ± 0.23
340.0[b]	64.06 ± 0.27	500.0	51.95 ± 0.28
360.0[b]	62.45 ± 0.23	520.0	50.54 ± 0.37
380.0[b]	60.87 ± 0.22	540.0	49.13 ± 0.47
400.0	59.32 ± 0.22	560.0	47.74 ± 0.58
420.0	57.79 ± 0.20	580.0[b]	46.37 ± 0.73
440.0	56.31 ± 0.20	600.0[b]	44.99 ± 0.91
460.0	54.83 ± 0.20	620.0[b]	43.6 ± 1.1
1-Nonyne			
280.0[b]	48.81 ± 0.18	400.0	39.65 ± 0.27
298.15[b]	47.34 ± 0.17	420.0	38.08 ± 0.38
300.0[b]	47.19 ± 0.17	440.0	36.42 ± 0.52
320.0	45.64 ± 0.17	460.0	34.65 ± 0.68
340.0	44.13 ± 0.15	480.0[b]	32.73 ± 0.86
360.0	42.65 ± 0.17	500.0[b]	30.7 ± 1.1
380.0	41.17 ± 0.20	520.0[b]	28.4 ± 1.3
Trimethylacetic Acid[c]			
290.0[b,d]	60.05 ± 0.28	400.0	50.88 ± 0.23
298.15[b,d]	59.39 ± 0.28	420.0	48.99 ± 0.28
300.0[b,d]	59.24 ± 0.28	440.0	46.95 ± 0.37
320.0	57.64 ± 0.25	460.0	44.75 ± 0.52
340.0	56.01 ± 0.23	480.0[b]	42.35 ± 0.70
360.0	54.36 ± 0.22	500.0[b]	39.75 ± 0.91
380.0	52.66 ± 0.22	520.0[b]	36.9 ± 1.2
Trimethylacetic Anhydride			
298.15[b]	56.06 ± 0.25	440.0	44.01 ± 0.37
300.0[b]	55.88 ± 0.23	460.0	42.19 ± 0.50
320.0[b]	54.09 ± 0.22	480.0	40.25 ± 0.67
340.0[b]	52.36 ± 0.20	500.0	38.16 ± 0.86
360.0	50.69 ± 0.18	520.0[b]	35.9 ± 1.1
380.0	49.05 ± 0.18	540.0[b]	33.4 ± 1.4
400.0	47.41 ± 0.22	560.0[b]	30.8 ± 1.7
420.0	45.74 ± 0.27		
Ethyl Trimethyl Acetate			
280.0[b]	42.72 ± 0.15	380.0	35.42 ± 0.30
298.15[b]	41.41 ± 0.15	400.0	33.82 ± 0.42
300.0[b]	41.27 ± 0.13	420.0	32.14 ± 0.57
320.0	39.84 ± 0.13	440.0[b]	30.34 ± 0.75
340.0	38.40 ± 0.17	460.0[b]	28.4 ± 1.0
360.0	36.94 ± 0.22	480.0[b]	26.3 ± 1.2

[a] Uncertainty intervals are twice the standard deviation. [b] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner equation. [c] Values calculated assuming a monomeric gas-phase, that is, NO cyclic dimerization similar to that present in other aliphatic carboxylic acids (See, for example, ref 81). [d] The value at this temperature represents the metastable (supercooled) liquid.

the critical pressure. A value for ω was obtained from the vapor-pressure fitting parameters and a corresponding value of ρ_c derived from the density measurement at 298.15 K, or at 320 K for *trans*-methyl cinnamate and trimethylacetic acid, listed in Table 2. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,[47] and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.[48] This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene.[36] Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients are assumed to be 10% of the respective numerical values. Derived enthalpies of vaporization are reported in Table 12. For $p > 1$ bar, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

Ideal-Gas Enthalpies of Formation. Table 13 summarizes the thermochemical property measurements and derived ideal-gas standard enthalpies of formation for all the compounds of this study. The enthalpies of vaporization, $\Delta_l^g H_m$, at 298.15 K reported in Table 12 were con-

Table 13. Thermochemical Properties at 298.15 K (R = 8.314 51 J·K^{-1}·mol^{-1} and p° = 101.325 kPa)

compd	$\Delta_f H^\circ_m$(c)/kJ·mol^{-1}	$\Delta_c^l H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$(l)/kJ·mol^{-1}	$\Delta_l^g H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$(g)/kJ·mol^{-1}
methyl methacrylate			−375.07 ± 0.54	38.97 ± 0.13	−336.1 ± 0.6
trans-methyl cinnamate	−302.21 ± 0.88	32.0 ± 1.0	−270.2 ± 1.3	69.99 ± 0.43	−200.2 ± 1.4
α-methyl cinnamaldehyde			−73.16 ± 1.08	67.52 ± 0.35	−5.6 ± 1.1
1-nonyne			15.67 ± 1.02	47.34 ± 0.17	63.0 ± 1.0
trimethylacetic acid	−568.91 ± 0.60	2.4 ± 0.3	−566.5 ± 0.7	59.39 ± 0.28[a]	−507.1 ± 0.8
trimethylacetic anhydride			−786.16 ± 1.06	56.06 ± 0.25	−730.1 ± 1.1
ethyl trimethyl acetate			−560.02 ± 0.82	41.41 ± 0.15	−518.6 ± 0.8

[a] Value calculated assuming a monomeric gas-phase, that is, NO cyclic dimerization similar to that present in other aliphatic carboxylic acids (See, for example, ref 81).

verted to the corresponding values for the ideal gas, $\Delta_l^g H^\circ_m$, using estimated ($H^\circ - H$) values for the real gas at its saturation vapor pressure at 298.15 K. The estimates were calculated using eq 20 of Chirico et al.[49] and virial coefficients derived as described above. For methyl methacrylate, the gas-imperfection correction was 0.05 kJ·mol^{-1} at 298.15 K. For all the other compounds of this study, the corrections were calculated to be negligibly small.

Discussion

Methyl Methacrylate. Two previous determinations of the enthalpy of combustion of methyl methacrylate[50,51] were found in a search of the literature through June 1997. Neither determination was abstracted by Pedley in either of his recent thermochemical data compilations.[9,10] The values for the enthalpies of combustion obtained by Iwai, $\Delta_c H^\circ_m$($C_5H_8O_2$(l), 298.15 K) = −(2704.2) kJ·mol^{-1}, and by Vilcu and Perisanu, $\Delta_c H^\circ_m$($C_5H_8O_2$(l), 298.15 K) = −(2724.6 ± 4.0) kJ·mol^{-1}, are both considerably lower than that, $\Delta_c H^\circ_m$($C_5H_8O_2$(l), 298.15 K) = −(2735.80 ± 0.46) kJ·mol^{-1}, obtained in this research. Lack of experimental details in the earlier papers prevented any determination of possible reasons for the large deviations. Vilcu and Perisanu[51] also report a value of −(108 ± 5.0) kJ·mol^{-1} for the enthalpy of hydrogenation of methyl methacrylate to 2-methylpropionic acid methyl ester in contrast to an earlier determination[52] of $\Delta_r H^\circ_m$($C_5H_8O_2$(g), 355 K) = −(119.8 ± 0.2) kJ·mol^{-1} resulting in the same product. The absence of a reliable measured enthalpy of formation for 2-methylpropionic acid methyl ester precludes determination of the enthalpy of formation of methyl methacrylate via the enthalpies of hydrogenation. For further discussion, see below.

As noted above, the sample of methyl methacrylate used in the ebulliometric vapor-pressure measurements initially formed a glass at ~403 K which quickly became a polymer blocking the apparatus. Guseinov et al.[53] noted during their *PVT* hydrostatic weighing method study on methyl methacrylate that at >425 K "strong polymerization occurred". Because of the ease of polymerization on heating, all literature references to the critical properties of methyl methacrylate are estimates. In this research, T_c = (563 ± 5) K with ρ_c = (318 ± 20) kg·m^{-3} and p_c = (3670 ± 300) kPa are used.

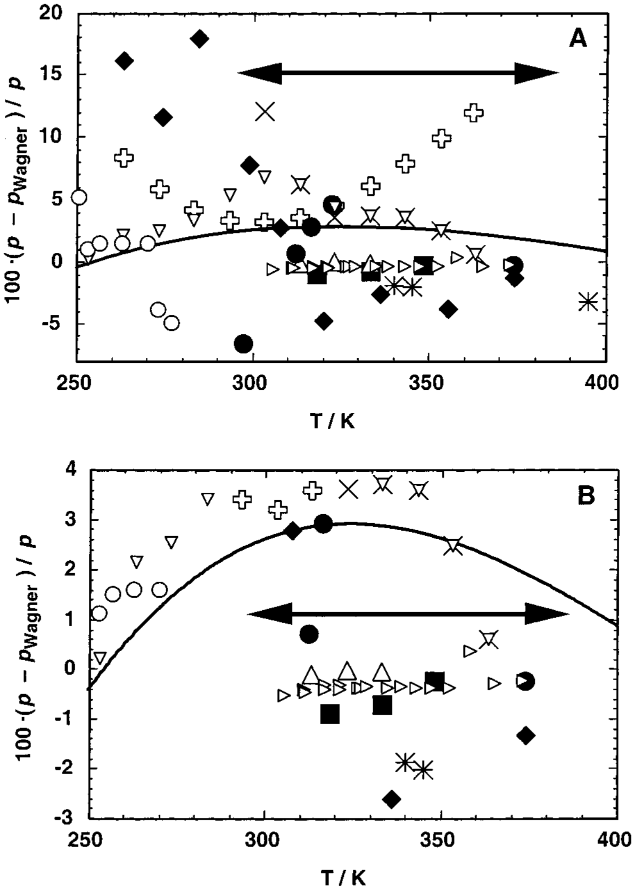

Figure 3. Comparison of literature vapor pressures for methyl methacrylate with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (Table 7). The solid line represents the DIPPR Project 801 correlation equation.[64]). Key: (●) Barnes;[54] (◆) Stull;[55] (×) Blout and Mark;[56] (○) Bywater;[57] (▽) Riddle;[58] (plus sign) Brockhaus and Jenckel;[59] (∗) Engineering Science Data;[60] (triangle pointing right) Boublík and Aim;[61] (△) Yu et al.;[62] (□) Hull and Lu.[63] Part B is an expansion of the deviation scale to aid in differentiation of the data.

Figure 3 compares sets of vapor-pressure measurements on methyl methacrylate reported in the literature[54−64] with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. In the abstract for the Brockhaus and Jenckel[59] reference in *Chemical Abstracts* (CA 51 23683), the vapor-pressure equation given for methyl methacrylate is in error. Instead of log p = (8.40 − 9320)/4.75T, it should read log p = (8.40 − 9320)/4.57T, since 2.303R approximates 4.57 not 4.75. The values reported by Stull in his 1947 compilation[55] appear to be unusually scattered with deviations ranging from approximately 20% high to 8% low. In agreement with the comments by Bywater,[57] the values for the vapor pressure given by Blout and Mark in their 1949 monograph *Monomers*[56] for temperatures less than 320 K "would appear to be in error probably due to inadequate degassing of the sample." Bywater[57] used a variation of the method due to Ramsey and Young[65] to obtain vapor-pressure measurements for methyl methacrylate both above and below the melting point. As shown in Figure 3, over most of the temperature range, agreement between Bywater's measurements and values extrapolated using the Wagner equation (eq 5) and the parameters listed in Table 10 is as good as would be expected, especially in the region below 270 K. Within the range of the vapor-pressure measurements obtained in this research (295 K to 386 K: 4 kPa to 143.2 kPa), agreement with the results of Boublík and Aim reported in the text by Boublík et al.[61] is excellent with deviations between the data sets averaging only 0.4%. Across the whole temperature range depicted in Figure 3 (250 K to 400 K), agreement of values of the vapor pressure obtained using the Wagner equation (eq 5) and the parameters listed in Table 10 with those derived using the DIPPR Project 801 correlation equation[64] is also good.

Brockhaus and Jenckel[59] list an equation representing the variation of density with temperature for methyl methacrylate in the region 295 K to 354 K. The value for the density obtained in this research at 298.15 K from the ampule filling procedure, 937 kg·m^{-3}, is in good agreement with the value, 938 kg·m^{-3}, obtained using the Brockhaus and Jenckel equation. This reference is not given in the compilation by Daubert et al.[64] and hence was not used in the derivation of the DIPPR Project 801 correlation equation for the liquid-phase saturation density. The equation

$$\rho/\mathrm{kg{\cdot}m^{-3}} = 318.0 - 64.7(1 - T_r)^{1/3} + 1800(1 - T_r)^{2/3} - 888.4(1 - T_r) + ... \quad (10)$$

where $T_r = T/T_c$ with $T_c = 563$ K is a good representation (±0.01%) of the saturation line isotherm from the *PVT* measurements of Guseinov et al.[53] (Note that there is a typographical error in Table 1 of ref 53; the density at 311.48 K and 0.1 MPa should read 923.4 kg·m^{-3} not 932.4 kg·m^{-3}.)

Estimation of the ideal-gas enthalpy of formation of methyl methacrylate follows, using the following group parameters derived within the DIPPR Project 871:

C−(O)(H)$_3$	−42.25
O−(CO)(C)	−179.70
CO−(O)(C$_d$)	−129.90
C$_d$−(C$_d$)(CO)(C)	31.40
C−(C$_d$)(H)$_3$	−42.25
C$_d$−(C$_d$)(H)$_2$	26.21

Hence,

$$\Delta_f H^\circ_m(C_5H_8O_2(g), 298.15\ K) = -336.49\ kJ{\cdot}mol^{-1}$$

This is in excellent agreement with the value $\Delta_f H^\circ_m$($C_5H_8O_2$(g), 298.15 K) = −(336.1 ± 0.6) kJ·mol^{-1} obtained in this research (Table 13). The result lends confidence to the self-consistency of the listed group parameter values.

For 2-methylpropionic acid methyl ester (the initial hydrogenation product of methyl methacrylate; see above), group additivity gives

C−(O)(H)$_3$	−42.25
O−(CO)(C)	−179.70
CO−(O)(C)	−146.96
C−(C)$_2$(CO)(H)	−7.54
2C−(C)(H)$_3$	−42.25 × 2 = −84.50

hence

$$\Delta_f H^\circ_m(C_5H_{10}O_2(g), 298.15\ K) = -460.95\ kJ{\cdot}mol^{-1}$$

The ideal-gas enthalpy of hydrogenation is estimated as −124.46 kJ·mol^{-1} [−460.95 − (−336.49)], which supports the determination of Dolliver et al.,[52] $\Delta_r H^\circ_m$($C_5H_8O_2$, 355 K) = −(119.8 ± 0.2) kJ·mol^{-1}, over that of Vilcu and Perisanu,[51] −(108 ± 5.0) kJ·mol^{-1}.

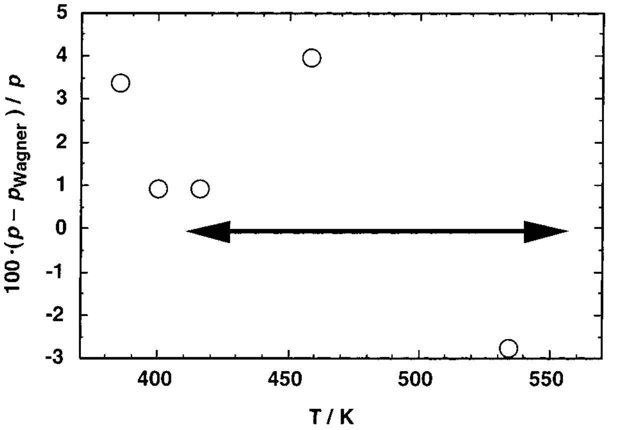

Figure 4. Comparison of literature vapor pressures for *trans*-methyl cinnamate with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (Table 7). Key: (○) von Rechenberg.[66]

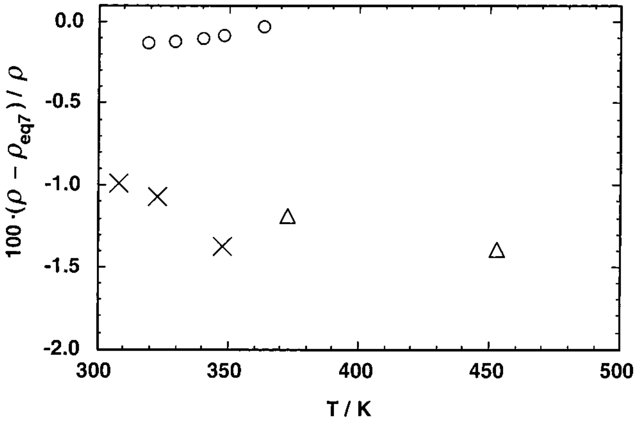

Figure 5. Comparison of literature saturation densities for *trans*-methyl cinnamate with values obtained by extended corresponding states (eq 9) and the parameters given in Table 10. Key: (×) Jaeger;[67] (○) Sugden and Whittaker;[68] (△) Albert.[69]

trans-Methyl Cinnamate. Other than 6 single-temperature density measurements, approximately 50 melting point determinations, and approximately the same number of single-point boiling-point determinations found in a Beilstein and *Chemical Abstracts* search through June 1997, the only other thermochemical or thermophysical property measurements found for *trans*-methyl cinnamate were measurements of vapor pressure versus temperature (385 K to 534 K) reported by von Rechenberg[66] and the variation of saturated liquid-phase density with temperature.[67−69] Figure 4 compares the vapor-pressure measurements on *trans*-methyl cinnamate reported by von Rechenberg[66] with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. Agreement is good and within the probable error limits of the earlier measurements. Figure 5 compares literature values for the density of *trans*-methyl cinnamate[67−69] with values calculated using extended corresponding states (eq 7) and the parameters listed in Table 10. The density obtained (Table 2) from measurements of the volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, 1071 kg·m^{-3} at 320 K, was used to determine ρ_c, and consequently, matches exactly that derived using eq 9. Agreement of the calculated densities with the measurements of Sugden and Whittaker[68] is excellent.

Estimation of the ideal-gas enthalpy of formation of *trans*-methyl cinnamate follows, using the following group parameters derived within the DIPPR Project 871:

$C-(O)(H)_3$	−42.25
$O-(CO)(C)$	−179.70
$CO-(O)(C_d)$	−129.90
$C_d-(C_d)(CO)(H)$	25.90
$C_d-(C_d)(C_b)(H)$	34.20
$C_b-(C_b)_2(C_d)$	23.785
$C_b-(C_b)_2(H)$	13.82 × 5 = 69.10

Hence

$$\Delta_f H_m^\circ(C_{10}H_{10}O_2(g), 298.15\ K) = -198.9\ kJ\cdot mol^{-1}$$

This is in excellent agreement with the value $\Delta_f H_m^\circ(C_{10}H_{10}O_2(g), 298.15\ K) = -(200.2 \pm 1.4)\ kJ\cdot mol^{-1}$ obtained in this research (Table 13). The result lends confidence to the self-consistency of the listed group parameter values.

α-Methyl Cinnamaldehyde. In a Beilstein and *Chemical Abstracts* search through June 1997, only one paper containing thermophysical property measurements over a temperature range for α-methyl cinnamaldehyde was found. Masood et al.[70] report density determinations without giving a temperature range. In addition, the equation listed for the variation of temperature for seven compounds including α-methyl cinnamaldehyde appears to have an error of sign, as the density *increases* with increasing temperature. Assuming the equation should read

$$\rho/g\cdot cm^{-3} = 1.0582 - 0.0008775(T/K - 273.2) \quad (11)$$

the calculated density at 298.15 K is 1036 $kg\cdot m^{-3}$, in good agreement with the value 1039 $kg\cdot m^{-3}$ obtained during the combustion calorimetry ampule-filling procedure and reported in Table 2. Using extended corresponding states (eq 9) and the parameters listed in Table 10, a value of 1057 $kg\cdot m^{-3}$ was estimated for the saturated liquid-phase density at 273.15 K, in agreement with the first constant in the above equation (eq 11).

Estimation of the ideal-gas enthalpies of formation of α-methyl cinnamaldehyde follows, using the following group parameters derived within the DIPPR Project 871:

$CO-(C_d)(H)$	−121.84
$C-(C_d)(H)_3$	−42.25
$C_d-(C_d)(CO)(C)$	31.40
$C_d-(C_d)(C_b)(H)$	34.20
$C_b-(C_b)_2(C_d)$	23.785
$C_b-(C_b)_2(H)$	13.82 × 5 = 69.10

Hence

$$\Delta_f H_m^\circ(C_{10}H_{10}O(g), 298.15\ K) = -5.6\ kJ\cdot mol^{-1}$$

This compares with the value $\Delta_f H_m^\circ(C_{10}H_{10}O(g), 298.15\ K) = -(5.6 \pm 1.1)\ kJ\cdot mol^{-1}$ obtained in this research (see Table 13).

1-Nonyne. Thermochemical measurements of the energy of combustion or reaction hydrogenation and hence formation of acetylenes are scare in the literature. Pedley in either of his recent thermochemical data compilations[9,10] lists enthalpies of formation for just five acetylenes: ethyne, propyne, 1-butyne, 2-butyne, and 3,3-dimethyl-1-butyne (the latter being restricted just to the condensed liquid phase). The enthalpies of formation were derived from the work of four groups: Conn et al.,[71] Prosen et al.,[72] Cordes and Günzler,[73] and Kupreev and Shimonaev,[74] who used hydrogenation reaction calorimetry, flame calorimetry, isomerization reaction calorimetry, and conventional liquid-phase combustion calorimetry, respectively. The Benson group-additivity functions $C_t-(C_t)(C)$, $C_t-(C_t)(H)$, and $C-(C_t)(C)(H)_2$ are derived from just the above four enthalpies of formation. (The absence of a standard enthalpy of vaporization for 3,3-dimethyl-1-butyne prevents an ideal-gas enthalpy of formation derivation for that compound and the group $C-(C_t)(C)_3$.) To solidify the group-additivity functions listed above, measurements were made on a 1-yne (non-1-yne). Future work on other acetylenes, for example, a 2-yne and a compound containing the $C-(C_t)(C)_2(H)$ group, is anticipated.

TRC[75] lists correlated values for the vapor pressure of 1-nonyne between 0.02 bar and 2 bar. The values are in serious disagreement with those obtained in this research (Table 7) and would point to an error in the derivation of the correlation. An earlier version of the *TRC Tables* (API-44 version[76]) lists a normal boiling point of 150.8 °C for 1-nonyne, in good agreement with the values listed in Table 7.

Literature values for the density of 1-nonyne in the temperature range 293 K to 358 K[77] agree within 0.1% with values calculated using extended corresponding states (eq 9) and the parameters listed in Table 10. The density obtained (Table 2) from measurements of the volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, 754 $kg\cdot m^{-3}$ at 298.15 K, was used to determine ρ_c and, consequently, matches exactly that derived using eq 9.

Estimation of the ideal-gas enthalpy of formation of 1-nonyne follows, using the following group parameters derived within the DIPPR Project 871:

$C_t-(C_t)(H)$	112.75
$C_t-(C_t)(C)$	115.35
$C-(C_t)(C)(H)_2$	−19.805
$C-(C)_2(H)_2$	−20.64 × 5 = −103.20
$C-(C)(H)_3$	−42.25

Hence

$$\Delta_f H_m^\circ(C_9H_{16}(g), 298.15\ K) = 62.9\ kJ\cdot mol^{-1}$$

The comparison with the value $\Delta_f H_m^\circ(C_9H_{16}(g), 298.15\ K) = (63.0 \pm 1.0)\ kJ\cdot mol^{-1}$ obtained in this research (Table 13) is excellent. The result lends confidence to the self-consistency of the Benson group additivity functions $C_t-(C_t)(C)$, $C_t-(C_t)(H)$, and $C-(C_t)(C)(H)_2$.

Note in Proof. After the submission of this report to the DIPPR 871 Committee and prior to submission to the Journal, attention was drawn to an additional reference to the enthalpies of formation of linear alkynes.[89] Rodgers et al.[89] measured the enthalpies of hydrogenation of all the isomeric linear alkynes containing 6 to 10 carbons. The measurements were made in hexane solution at ambient temperature. The authors give a long explanation as to why the reactions carried out approximately 7 mol % in hexane “could be considered as being essentially infinitely dilute and thermochemically not different from the gas-phase reaction.” Rodgers et al.[89] measured an enthalpy of hydrogenation of $-(291.0 \pm 1.9)\ kJ\cdot mol^{-1}$ for the reaction converting 1-nonyne to nonane in hexane solvent containing a small quantity of “10% Pd catalyst on charcoal.” Assuming their arguments regarding the equivalence of the measured enthalpy with that for the gas phase, and assuming an enthalpy of formation for nonane in the ideal-gas state of $\Delta_f H_m^\circ(C_9H_{20}(g), 298.15\ K) = -(228.2 \pm 0.7)\ kJ\cdot mol^{-1}$ (assigned; see ref 9), the enthalpy of hydrogena-

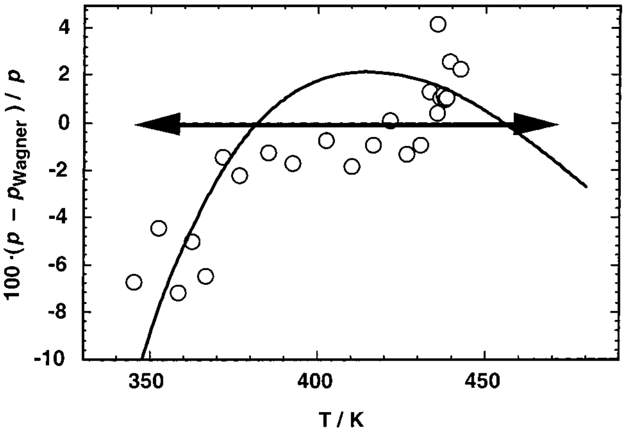

Figure 6. Comparison of literature vapor-pressure data for trimethylacetic acid with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (Table 7). The solid line represents the DIPPR Project 801 correlation equation.[64] Key: (○) TRC.[75]

tion of −(291.0 ± 1.9) kJ·mol^{-1} translates to an ideal-gas enthalpy of formation for 1-nonyne of $\Delta_f H_m^\circ(C_9H_{16}(g)$, 298.15 K) = (62.8 ± 2.0) kJ·mol^{-1}, in near perfect agreement with the value derived in this research, $\Delta_f H_m^\circ$(C_9H_{16}(g), 298.15 K) = (63.0 ± 1.0) kJ·mol^{-1}. Rodgers et al.[89] list mean enthalpies of hydrogenation for 1-ynes [−(291.4 ± 1.3) kJ·mol^{-1}], 2-ynes [−(273.6 ± 1.3) kJ·mol^{-1}], 3-ynes [−(271.1 ± 1.3) kJ·mol^{-1}], 4-ynes [−(269.4 ± 1.3) kJ·mol^{-1}], and a 5-yne [−(268.2 ± 2.1) kJ·mol^{-1}]. Using the group parameters given in refs 4 and 5, the corresponding calculated ideal-gas enthalpies of hydrogenation are −290.4 kJ·mol^{-1} for the 1-ynes, −271.5 kJ·mol^{-1} for the 2-ynes, and −271.9 kJ·mol^{-1} for the 3-ynes and above, in excellent agreement considering the assumptions listed above.

Trimethylacetic Acid. One previous determination of the enthalpy of combustion of trimethylacetic acid[78] was found in a search of the literature through June 1997. The value for the enthalpy of combustion obtained by Hancock et al., $\Delta_c H_m^\circ(C_5H_{10}O_2$(cr), 298.15 K) = −(2832.1 ± 5.9) kJ·mol^{-1}, is, within the large uncertainty interval, the same as that, $\Delta_c H_m^\circ(C_5H_{10}O_2$(cr), 298.15 K) = −(2827.79 ± 0.52) kJ·mol^{-1}, obtained in this research. Pedley, in both of his recent thermochemical data compilations,[9,10] erroneously lists the Hancock et al. value as being for the liquid phase.

Singh and Glicksman[79] used a high-purity sample of trimethylacetic acid (>99.9995 mol % pure) to determine the heat capacity, density, and viscosity as functions of temperature in the region close to the melting point. The melting point and heat-capacity equations representing both the solid and liquid phases obtained by Singh and Glicksman are in excellent agreement with the values reported in Table 8. The enthalpy of fusion $\Delta_{cr}^{l}H_m(C_5H_{10}O_2$, 309.1 K) = (2.3 ± 0.2) kJ·mol^{-1} obtained in this research is also in excellent agreement with the value $\Delta_{cr}^{l}H_m$($C_5H_{10}O_2$, 309.1 K) = (2.268 ± 0.046) kJ·mol^{-1} of Singh and Glicksman.[79]

Figure 6 compares sets of vapor-pressure data on trimethylacetic acid reported in the literature[75,64] with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. At temperatures greater than 370 K, agreement of values of the vapor pressure obtained using the Wagner equation (eq 5) and the parameters listed in Table 10 with those derived using the DIPPR Project 801 correlation equation[64] is within the assigned uncertainty limits on the 801 Project equation. Below 370 K, the DIPPR correlation gives too much weight to the TRC[75] correlation.

de Kruif and Oonk[80] used combined torsion- and weighing-effusion techniques to measure the saturation vapor pressures of seven carboxylic acids as a function of temperature. Results are given for solid trimethylacetic acid in the temperature region 242 K to 258 K. de Kruif and Oonk derive enthalpies of sublimation of $\Delta_{cr}^{g}H_m(C_5H_{10}O_2$, 250.52 K) = (78.4 ± 2) kJ·mol^{-1} and $\Delta_{cr}^{g}H_m(C_5H_{10}O_2$, 298.15 K) = (73.2 ± 2) kJ·mol^{-1}, respectively. The latter value is in very poor agreement with the value derived in this research, $\Delta_{cr}^{g}H_m(C_5H_{10}O_2$, 298.15 K) = (61.8 ± 0.4) kJ·mol^{-1} (see Tables 8, 12, and 13). The large difference may be related to the presence of the solid−solid phase transition at 278.3 K, as noted by Singh and Glicksman.[79] Singh and Glicksman list a value of (8.2 ± 0.1) kJ·mol^{-1} for the enthalpy of the transition that accounts for some of the discrepancy in the enthalpies of sublimation. In addition, the enthalpies of vaporization and sublimation derived in this research all assume a monomeric carboxylic acid in the gas phase. Earlier research on the vaporization of carboxylic acids by Jasperson et al.[81] (formic, C_3 through C_6 *n*-acids, acrylic, and methacrylic acids) in the DIPPR 832 Project shows the presence of a significant quantity of cyclic dimer in the gas phase at ambient temperature. Further measurements in the region between 260 K and 300 K accompanied by analysis of the vapor phase will be required to fully elucidate the situation.

Bearing in mind the uncertainty in the actual values for the enthalpies of vaporization and sublimation of trimethylacetic acid, estimation of the ideal-gas enthalpies of formation of trimethylacetic acid follows, using the following group parameters derived within the DIPPR Project 871:

O−(CO)(H)	−243.25
CO−(O)(C)	−146.96
C−(CO)(C)$_3$	5.90
3C−(C)(H)$_3$	−42.25 × 3 = −126.75
one 1,4 gauche interaction	4.0

Hence

$$\Delta_f H_m^\circ(C_5H_{10}O_2(g), 298.15\ K) = -507.1\ kJ\cdot mol^{-1}$$

This compares with the value $\Delta_f H_m^\circ(C_5H_{10}O_2$(g), 298.15 K) = −(507.1 ± 0.8) kJ·mol^{-1} obtained in this research (Table 13). The presence of any significant quantity of dimer in the gas phase at 298.15 K will not improve this near perfect agreement.

Note in Proof. After the submission of this report to the DIPPR 871 Committee and prior to submission to the Journal, two additional papers on the thermochemical and thermophysical properties of trimethylacetic acid have been published.[82,83] Verevkin[82] measured the vapor pressure by the transpiration method in the temperature range 278.3 K to 303.2 K, deriving the enthalpy of sublimation $\Delta_{cr}^{g}H_m$($C_5H_{10}O_2$, 298.15 K) = (62.09 ± 0.55) kJ mol^{-1}, in excellent agreement with that obtained in this research, $\Delta_{cr}^{g}H_m$($C_5H_{10}O_2$, 298.15 K) = (61.8 ± 0.4) kJ mol.$^{-1}$ The enthalpy of fusion $\Delta_{cr}^{l}H_m(C_5H_{10}O_2$, 309.1 K) = (2.3 ± 0.2) kJ·mol^{-1} obtained in this research is also in excellent agreement with the value $\Delta_{cr}^{l}H_m(C_5H_{10}O_2$, 309.0 K) = (2.38 ± 0.21) kJ·mol^{-1} of Verevkin.[82] Ribeiro da Silva et al.[83] report the measurement of the energies of combustion and hence derived enthalpies of formation of three branched alkyl carboxylic acids including trimethylacetic acid. The value for the enthalpy of combustion obtained by Ribeiro da Silva et al., $\Delta_c H^\circ_m(C_5H_{10}O_2(cr), 298.15\ K) = -(2828.76 \pm 0.90)\ kJ \cdot mol^{-1}$, is in almost perfect agreement with that, $\Delta_c H^\circ_m(C_5H_{10}O_2(cr), 298.15\ K) = -(2827.79 \pm 0.52)\ kJ \cdot mol^{-1}$, obtained in this research. It is unfortunate that Ribeiro da Silva et al.[83] use the enthalpy of sublimation of de Kruif and Oonk[80] to derive a gas-phase enthalpy of formation which (see their Table 4) differs from the group-additivity estimate by 10 $kJ \cdot mol^{-1}$. As noted above, a single gauche interaction energy of 4 $kJ \cdot mol^{-1}$ is sufficient to get agreement between the experimentally measured value and the additivity calculation.

Trimethylacetic Anhydride. With the exception of a paper on the enthalpies of hydrolysis of anhydrides[84] and approximately a couple of dozen single-point boiling-point determinations, no other references to thermochemical or thermophysical property measurements were found in a Beilstein and *Chemical Abstracts* search through June 1997. Conn et al.[84] measured the enthalpy of hydrolysis at 303 K of eleven acid anhydrides including trimethylacetic anhydride. From the measurements, corrected to 298.15 K, the enthalpy of the following reaction was derived:

$$((CH_3)_3CO)_2O(l) + H_2O(l) \rightarrow 2(CH_3)_3COOH(cr)$$

$$\Delta_r H^\circ_m(298.15\ K) = -(63.5 \pm 1.0)\ kJ \cdot mol^{-1}$$

Combination of that enthalpy of reaction with the enthalpy of formation of crystalline trimethylacetic acid, $\Delta_f H^\circ_m(C_5H_{10}O_2(cr), 298.15\ K) = -(568.91 \pm 0.60)\ kJ \cdot mol^{-1}$, (see Tables 6 and 13) and the enthalpy of formation of liquid water, $\Delta_f H^\circ_m(H_2O(l), 298.15\ K) = -(285.830 \pm 0.042)\ kJ \cdot mol^{-1}$, as assigned by CODATA[34] gives $\Delta_f H^\circ_m(C_8H_{18}O_3(l), 298.15\ K) = -(788.5 \pm 1.3)\ kJ \cdot mol^{-1}$. This is in excellent agreement with the value $\Delta_f H^\circ_m(C_8H_{18}O_3(l), 298.15\ K) = -(786.16 \pm 1.06)\ kJ \cdot mol^{-1}$ obtained in the combustion calorimetric measurements (see Tables 6 and 13). A weighted mean of combustion calorimetric measurements and the value derived using the results of Conn et al.,[84] $\Delta_f H^\circ_m(C_8H_{18}O_3(l), 298.15\ K) = -(787.4 \pm 1.0)\ kJ \cdot mol^{-1}$, is recommended. Using this recommended value in combination with the enthalpy of vaporization at 298.15 K listed in Table 12 gives $\Delta_f H^\circ_m(C_8H_{18}O_3(g), 298.15\ K) = -(731.3 \pm 1.0)\ kJ \cdot mol^{-1}$.

Estimation of the ideal-gas enthalpies of formation of trimethylacetic anhydride follows, using the following group parameters derived within the DIPPR Project 871:

$O-(CO)_2$	-194.60
$2CO-(O)(C)$	$-146.96 \times 2 = -293.92$
$2C-(CO)(C)_3$	$5.9 \times 2 = 11.80$
$6C-(C)(H)_3$	$-42.25 \times 6 = -253.50$

Hence

$$\Delta_f H^\circ_m(C_8H_{18}O_3(g), 298.15\ K) = -730.2\ kJ \cdot mol^{-1}$$

This compares with the value $\Delta_f H^\circ_m(C_8H_{18}O_3(g), 298.15\ K) = -(731.3 \pm 1.0)\ kJ \cdot mol^{-1}$ obtained above.

Ethyl Trimethyl Acetate. Three papers on the determination of the enthalpy of combustion of ethyl trimethyl acetate[78,85,86] were found in a search of the literature through June 1997. The values for the enthalpy of combustion obtained by Hancock et al.,[78] $\Delta_c H^\circ_m(C_7H_{14}O_2(l), 298.15\ K) = -(4180.3 \pm 3.3)\ kJ \cdot mol^{-1}$, and by Verevkin et al.,[85,86] $\Delta_c H^\circ_m(C_7H_{14}O_2(l), 298.15\ K) = -(4188.5 \pm 1.0)\ kJ \cdot mol^{-1}$, differ somewhat from the value, $\Delta_c H^\circ_m(C_7H_{14}O_2(l), 298.15\ K) = -(4195.36 \pm 0.70)\ kJ \cdot mol^{-1}$, obtained in this research (see Tables 5 and 6). Small quantities of water, 0.1 to 0.2 mol %, present in the earlier combustion samples could account for the differences.

As outlined above, values for the critical properties $T_c = (566 \pm 1)$ K with $\rho_c = (280 \pm 10)\ kg \cdot m^{-3}$ and $p_c = (2950 \pm 100)$ kPa were derived for ethyl trimethyl acetate. Using the estimate scheme due to Joback,[42] the corresponding estimated values are $T_c = 565$ K with $\rho_c = 294\ kg \cdot m^{-3}$ and $p_c = 2870$ kPa. In a search of the literature, no experimentally determined critical point values were obtained for comparison.

In a study of the enthalpies of solution of mono-, di-, and triesters in water, Nilsson and Wadsö[87] measured the heat capacity of ethyl trimethyl acetate using a drop-heat capacity calorimeter. They list a value of C_{sat} of $(30.22 \pm 0.02)R$ at 298.15 K. This agrees within the uncertainty interval (±1%) with the value of $30.0R$ at 300 K derived from the two-phase DSC heat-capacity measurements reported here (Table 12).

Wadsö[88] determined the enthalpy of vaporization of ethyl trimethyl acetate using a vaporization calorimeter. The value $\Delta_l^g H_m(C_7H_{14}O_2, 298.15\ K) = (41.25 \pm 0.13)\ kJ \cdot mol^{-1}$ is in good agreement with that derived from the Wagner-equation fit using the Clapeyron equation (eq 6 above), $\Delta_l^g H_m(C_7H_{14}O_2, 298.15\ K) = (41.41 \pm 0.15)\ kJ \cdot mol^{-1}$ (Table 12).

Estimation of the ideal-gas enthalpies of formation of ethyl trimethyl acetate follows, using the following group parameters derived within the DIPPR Project 871:

$4C-(C)(H)_3$	$-42.25 \times 4 = -169.00$
$C-(C)(O)(H)_2$	-33.91
$O-(CO)(C)$	-179.70
$CO-(O)(C)$	-146.96
$C-(CO)(C)_3$	5.90
one 1,4 gauche interaction	4.0

Hence

$$\Delta_f H^\circ_m(C_7H_{14}O_2(g), 298.15\ K) = -519.7\ kJ \cdot mol^{-1}$$

This compares with the value $\Delta_f H^\circ_m(C_7H_{14}O_2(g), 298.15\ K) = -(518.6 \pm 0.8)\ kJ \cdot mol^{-1}$ obtained in this research (Table 13).

Conclusions

Confirmation of Literature Enthalpies of Formation, Revised Groups, and Interaction Terms. The experimentally derived ideal-gas enthalpies of formation of methyl methacrylate, *trans*-methyl cinnamate, and α-methyl cinnamaldehyde all confirm the group-additivity parameters used in the respective tabulated values. In addition, the estimation of an ideal-gas enthalpy of formation for 2-methylpropionic acid methyl ester, $\Delta_f H^\circ_m(C_5H_{10}O_2(g), 298.15\ K) = -461\ kJ \cdot mol^{-1}$, leads credence to the 1938 Dolliver et al.[52] measured enthalpy of hydrogenation of methyl methacrylate over that of a later study by Vilcu and Perisanu in 1980.[51]

The scarcity of thermochemical measurements on acetylenes was noted in this paper. The measured ideal-gas enthalpy of formation of 1-nonyne, $\Delta_f H^\circ_m(C_9H_{16}(g), 298.15\ K) = -(63.0 \pm 1.0)\ kJ \cdot mol^{-1}$, confirms the validity of the Benson group-additivity parameters for 1-ynes. Further measurements on 2-ynes and so forth are required to confirm and derive further group parameters.

Thermochemical property measurements on trimethylacetic acid, trimethylacetic anhydride, and ethyl trimethyl acetate led to confirmation of the Benson group parameters used in the corresponding estimations. Agreement between a value derived from measurements of the enthalpy of hydrolysis[84] and a value calculated using the energy of combustion measured in this research (Tables 4−6) is excellent. Combining both sets of results, the value $\Delta_f H^\circ_m(C_8H_{18}O_3(l), 298.15\ K) = -(731.1 \pm 1.0)\ kJ\cdot mol^{-1}$ is recommended for the standard enthalpy of formation of trimethylacetic anhydride.

In addition, values of the critical properties [$T_c = (566 \pm 1)$ K with $\rho_c = (280 \pm 10)\ kg\cdot m^{-3}$ and $p_c = (2950 \pm 100)$ kPa] were derived for ethyl trimethyl acetate

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