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Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for 2-Aminoisobutyric Acid (2-Methylalanine), Acetic Acid, (*Z*)-5-Ethylidene-2-norbornene, Mesityl Oxide (4-Methyl-3-penten-2-one), 4-Methylpent-1-ene, 2,2′-Bis(phenylthio)propane, and Glycidyl Phenyl Ether (1,2-Epoxy-3-phenoxypropane)

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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 (DSC) heat-capacity measurements. Ideal-gas enthalpies of formation of acetic acid, (*Z*)-5-ethylidene-2-norbornene, mesityl oxide (4-methyl-3-penten-2-one), 4-methylpent-1-ene, glycidyl phenyl ether (1,2-epoxy-3-phenoxypropane), and 2,2′-bis(phenylthio)propane are reported. An enthalpy of formation of 2-aminoisobutyric acid (2-methylalanine) in the crystalline phase was determined. Using a literature value for the enthalpy of sublimation of 2-aminoisobutyric acid, a value for the ideal-gas enthalpy of formation was derived. An enthalpy of fusion was determined for 2,2′-bis(phenylthio)propane. 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 except acetic acid. For mesityl oxide and 4-methylpent-1-ene, critical temperatures and critical densities were determined from the DSC results and corresponding critical pressures derived from the fitting procedures. Group-additivity parameters and ring strain energies useful in the application of 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 through some of its member industrial organizations. The objective of this ongoing (as of 1997) 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 eighth 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 1993 and subsequent communications, in which representatives of the DOE Bartlesville Project Office, DIPPR, and 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 Abstract 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 [2-aminoisobutyric acid and 2,2′-bis(phenylthio)propane] were both crystalline solids. Hence the derivation of ideal-gas standard energies of formation for each of the compounds required experimental measurements in addition to the determination of the standard enthalpies of combustion.

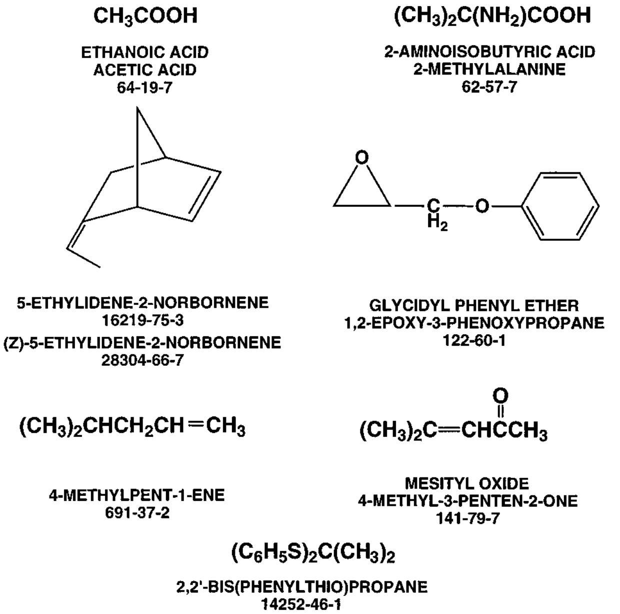

Figure 1. Structural formula, common names, Chemical Abstract Service names (provided by the authors), and Chemical Abstract Services Registry Numbers (provided by the authors) for the compounds studied in this research.

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

compound (state)	$\Delta_c U^\circ_m$	vapor pressure	heat capacity	T_c, ρ_c[b]
acetic acid (l)	x			
2-aminoisobutyric acid (cr)	x	x		
(*Z*)-5-ethylidene-2-norbornene (l)	x	x	x	
1,2-epoxy-3-phenoxypropane (l)	x	x	x	
mesityl oxide (l)	x	x	x	x
4-methylpent-1-ene (l)	x	x	x	x
2,2′-bis(phenylthio)propane (cr)	x	x	x	

[a] Measurements made are denoted by x. [b] From DSC measurements.

A listing of the auxilliary 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 sample whose purity is >99.95 mol % is a goal of this project.

There is in the literature numerous sets of Benson Group Parameters, Benson (1968), Benson et al. (1969), Cox and Pilcher (1970), Benson (1976), Reid et al. (1987), Cohen and Benson (1993), Domalski and Hearing (1995), and Cohen (1996), to name just a few. In addition there are various other schemes that use extensions of the methodology, e.g., Pedley et al. (1986) and Pedley (1994). Also, in several papers, e.g., Eigenmann et al. (1973), corrections to earlier work [in that case Benson (1968)] 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 Benson (1976). In Reid et al. (1987) the corresponding value is also −7.95 kJ but is listed as −1.17 kJ in Domalski and Hearing (1995) and −10.0 kJ in Cohen (1996). To complicate the picture even more, it is believed that Reid et al. (1987) used a value of 4.1868 and not 4.184 to convert from the thermochemical calorie used by Benson in his 1976 text to the values reported in their text. By missing the Eigenmann et al. (1973) reference, Reid et al. (1987) 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. Cohen and Benson (1993) and Cohen (1996) 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 e.g., 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. (1987) values falling back on the Benson (1976) 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 chemical engineer practicing his craft, and any errors in that text are highlighted. [An author (W.V.S) believes most process-design simulation programs use Reid et al. (1987) for their group-addivity parameters.]

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 auxilliary 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 (Steele et al., 1996a−c) give detailed references to the experimental techniques and fitting procedures. Therefore, in this paper no details are given, and the reader is referred to Steele et al. (1996a−c) 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. Capillary gas chromatographic (CGC) analyses on the purchased samples gave an average purity of 98 mol % in agreement with Aldrich specifications. An exception was the mesityl oxide sample received from Aldrich. CGC analyses showed the sample of mesityl oxide (i.e., 4-methyl-3-penten-2-one) contained approximately 16% of isomesityl oxide (4-methyl-4-penten-2-one). The samples of acetic acid, (*Z*)-5-ethylidene-2-norbornene, 4-methylpent-1-ene, glycidyl phenyl ether, and the mesityl oxide were all purified by repeated spinning-band distillations. 2-Aminoisobutyric acid was purified by repeated recrystallization from ethanol followed by two sublimations at approximately 500 K under a high vacuum ($\sim 1 \cdot 10^{-5}$ kPa). The sulfur-containing compound, 2,2′-bis(phenylthio)propane (which was also a solid at ambient temperature) was zone refined (100 passes). CGC analyses of the samples used in the measurements gave purities of at least 99.95 mol % for each compound including the mesityl oxide. 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.

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 *n*-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. CGC analysis of the *n*-decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1991 relative atomic masses (IUPAC, 1993) and the gas constant, $R = 8.314\,51$ J·K^{-1}·mol^{-1}, adopted by CODATA (Cohen and Taylor, 1988). The platinum resistance thermometers and the quartz crystal thermometer used in these measurements were calibrated by

Table 2. Physical Properties at 298.15 K[a]

compound (state)	ρ/kg·m^{-3}	$10^7(\partial V/\partial T)_p$/ m^3·K^{-1}	C_p/R
acetic acid (l)	1044	0.62	14.8[b]
2-aminoisobutyric acid (cr)	1280	(0.3)	17.7
(*Z*)-5-ethylidene-2-norbornene (l)	902	1.3	24.3
1,2-epoxy-3-phenoxypropane (l)	1106	1.1	33.0
mesityl oxide (l)	850	1.2	23.6
4-methylpent-1-ene (l)	658	1.9	22.9
2,2′-bis(phenylthio)propane (cr)	1200	(0.3)	35.0

[a] Values in parentheses are estimates. [b] Martin and Andon (1982).

comparison with standard platinum resistance thermometers whose constants were determined at the National Institute for Standards and Technology (NIST) in the 1950s or early 1970s. All temperatures are reported in terms of ITS-90 (Goldberg and Weir, 1990; Mangum and Furukawa, 1990). 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,N,O compounds and C,H,S compounds at the National Institute for Petroleum and Energy Research have been described previously in Good (1969, 1972), Good and Smith (1969), Steele et al. (1988), and Hubbard et al. (1954) and Waddington et al. (1956), respectively.

A rotating-bomb calorimeter (laboratory designation BMR II) (Good et al., 1956) and a platinum-lined bomb (laboratory designation Pt-3b) (Good et al., 1959) with an internal volume of 0.3934 dm^3 were used with rotation in the fourth series of combustions, which included the sulfur-containing compound, and without rotation in the remaining series. Flexible borosilicate-glass ampules (Guthrie et al., 1952; Good, 1972) were used to confine the samples that were liquid at 298 K [acetic acid, (*Z*)-5-ethylidene-2-norbornene, 1,2-epoxy-3-phenoxypropane, mesityl oxide, and 4-methylpent-1-ene]. All experiments, subsequent to the first which defined the energy of combustion of the compound, were completed within 0.01 K of $T = 298.15$ K.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26\,434.0 \pm 3.0)$ J·g^{-1} under certificate conditions. Conversion to standard states (Hubbard et al., 1956) gives $-(26\,413.7 \pm 3.0)$ J·g^{-1} for $\Delta_c U^\circ_m/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in four separate series over a nine-month period as the purified compounds became available. Calibration experiments were interspersed with each series of measurements. Nitrogen oxides were not formed in the calibration experiments due to the high purity of the oxygen used and preliminary bomb flushing. The energy equivalent of the calorimeter, ϵ(calor), obtained during each calibration series is listed in Tables 3 and 4. The small changes in the energy equivalent between the various combustion series were due to small repairs to the bomb to cure leaking gaskets that develop with age and continual usage.

The auxilliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material, $\Delta_c U^\circ_m/M$ was $-(46\,042.5 \pm 1.8)$ J·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·g^{-1}. Information necessary for reducing 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 (Hubbard et al., 1956) is given in Table 2.

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 that were solid at 298.15 K {2-aminoisobutyric acid and 2,2′-bis(phenylthio)propane}. Values of the heat capacity of each sample at 298.15 K were measured using a differential-scanning calorimeter.

In the combustion of the sulfur-containing compound, 2,2′-bis(phenylthio)propane, the bomb initially contained 10 cm^3 of water. One atmosphere of air was left in the bomb, which was subsequently charged with pure oxygen to a total pressure of 3.04 MPa. In addition, rotation of the bomb was started at the “midtime of the combustion” (Waddington et al., 1956) and continued to the finish of the combustion experiments. This ensured a homogeneous solution of aqueous sulfuric acid in the bomb at the conclusion of the measurements. In the benzoic acid calibration measurements for this fourth series of combustions, rotation was also instituted to ensure exact consistency between the measurements.

In the 2,2′-bis(phenylthio)propane combustions the final bomb solutions were analyzed for nitric acid, nitrous acid, and total acids (Hubbard et al., 1954; Waddington et al.,

Table 3. Typical Combustion Experiments at 298.15 K for the C,H,O,N Compounds Studied ($p^\circ = 101.325$ kPa)[a,b]

	A	B	C	D	E	F
m'(compound)/g	0.995 796	1.523 235	0.712 865	0.995 808	0.838 760	0.647 394
m''(oil)/g	0.047 512		0.041 744	0.041 414	0.066 579	0.064 882
m'''(fuse)/g	0.001 971	0.002 236	0.002 555	0.001 937	0.002 874	0.002 370
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	38.469	19.363	38.470	38.470	34.568	38.468
ΔT/K[c]	0.996 98	2.000 04	2.007 69	2.010 85	2.000 11	2.008 46
ϵ(calor)/J·K^{-1}	16 772.7 ± 2.4	16 773.2 ± 0.6	16 773.2 ± 0.6	16 773.2 ± 0.6	16 773.2 ± 0.6	16 773.1 ± 0.5
ϵ(calor)(ΔT)/J	−16 722.1	−33 547.1	−33 675.5	−33 728.4	−33 548.3	−33 688.3
ϵ(cont)(ΔT)/J [d]	−21.9	−40.5	−44.2	−45.2	−45.0	−44.7
ΔU_{ign}/J	0.8	0.8	0.8	0.9	0.8	0.8
ΔU(corr std states)/J[e]	13.5	20.7	15.4	21.6	15.5	10.7
$\Delta U_{dec}(HNO_3)$/J		92.4				
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2 187.6		2 440.1	1 906.8	3 065.5	2 987.3
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	33.4	37.9	40.3	32.8	48.7	40.2
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−14 508.7	−33 435.8	−31 738.2	−31 811.6	−30 462.8	−30 694.0
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−14 570.1	−21 951.4	−44 522.1	−31 945.6	−36 318.9	−47 411.6

[a] A = acetic acid; B = 2-aminoisobutyric acid; C = (*Z*)-5-ethylidene-2-norbornene; D = 1,2-epoxy-3-phenoxypropane; E = mesityl oxide; and F = 4-methylpent-1-ene. [b] The symbols and abbreviations of this table are those of Hubbard et al. (1956) except as noted. [c] $\Delta T/\mathrm{K} = (T_i - T_f + \Delta T_{corr})/\mathrm{K}$. [d] $\epsilon_i(\mathrm{cont})(T_i - 298.15\ \mathrm{K}) + \epsilon_f(\mathrm{cont})(298.15\ \mathrm{K} - T_f + \Delta T_{corr})$. [e] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of Hubbard et al. (1956).

Table 4. Typical Combustion Experiment at 298.15 K for 2,2′-Bis(phenylthio)propane ($p° = 101.325$ kPa)[a]

2,2′-Bis(phenylthio)propane	
m'(compound)/g	0.925 594
m''(fuse)/g	0.002 367
$n_i(H_2O)$/mol	0.553 45
m(Pt)/g	32.077
ΔT/K[b]	2.003 30
ϵ(calor)/J·K^{-1}	16 776.5 ± 0.7
ϵ(calor)(ΔT)/J	−33 608.4
ϵ(cont)(ΔT)/J [c]	−116.4
ΔU_{ign}/J	0.8
ΔU(corr std states)/J[d]	23.5
$\Delta U_{dec}(HNO_3)$/J	44.9
$\Delta U_{dil}(H_2SO_4)$/J	−3.1
$-m''(\Delta_c U^\circ_m/M)$(fuse)/J	37.0
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−33 618.6
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−36 321.0

[a] The symbols and abbreviations of this table are those of Hubbard et al. (1956) except as noted. [b] $\Delta T/K = (T_i - T_f + \Delta T_{corr})/K$. [c] $\epsilon_i(cont)(T_i - 298.15\ K) + \epsilon_f(cont)(298.15\ K - T_f + \Delta T_{corr})$. [d] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of Hubbard et al. (1956).

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

Acetic Acid
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−14 570.1, −14 571.6, −14 577.6
−14 568.4, −14 572.3, −14 578.6
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −14 573.1 ± 1.7
2-Aminoisobutyric Acid
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−21 951.4, −21 953.3, −21 956.8
−21 960.4, −21 954.3, −21 959.6
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −21 956.0 ± 1.5
(Z)-5-Ethylidene-2-norbornene
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−44 522.1, −44 523.7, −44 525.6
−44 524.3, −44 520.9, −44 523.1
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −44 523.3 ± 0.7
1,2-Epoxy-3-phenoxypropane
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−31 945.6, −31 948.4, −31 944.5
−31 942.8, −31 946.7, −31 944.5
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −31945.4 ± 0.8
Mesityl Oxide
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−36 318.9, −36 316.4, −36 313.2
−36 316.7, −36 316.0
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −36 316.2 ± 0.9
4-Methylpent-1-ene
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−47 411.6, −47 408.5, −47 414.7
−47 416.9, −47 414.9, −47 412.4
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −47 413.2 ± 1.2
2,2′-Bis(phenylthio)propane
$\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})$
−36 321.0, −36 310.2, −36 309.3
−36 302.1, −36 308.9
$\langle\{(\Delta_c U^\circ_m/M)(compound)\}/(J{\cdot}g^{-1})\rangle$ −36 310.3 ± 3.0

[a] The uncertainties shown are 1 standard deviation of the mean. [b] All the energy of combustion measurements made for each compound are listed in this table.

1956). The amount of sulfuric acid was obtained by difference. No evidence of thermally significant amounts of SO_2 or of sulfuric acid attack on the borosilicate glass ampule or bomb was found. {Leaving the atmosphere of air in the platinum-lined bomb before charging to a total pressure of 3.04 MPa with pure oxygen ensured that all the sulfur was converted to SO_3 by the Contact Process [i.e., the industrial method of preparation of sulfuric acid (Harrer, 1969)].} No nitrous acid was observed in the combustions of the sulfur-containing compound.

Nitric acid, formed during combustions of the nitrogen-containing compound, 2-aminoisobutyric acid, was determined by titration with standard sodium hydroxide (Good and Moore, 1970). Carbon dioxide was also recovered from the combustion products of each experiment. (Due to the relatively large amount of water used to ensure a homogeneous solution of sulfuric acid in the 2,2′-bis(phenylthio)propane combustions, no CO_2 recoveries were made for that compound.) Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries (Good and Smith, 1969). The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. With the exception of 2,2′-bis(phenylthio)propane, where the results of the combustion measurements are based on the mass of sample used, all the reported values for energies and enthalpies of combustion are based on the mass of CO_2 recovered.

Results

Combustion Calorimetry. A typical combustion experiment for each C,H,O,N compound studied is summarized in Table 3. It is impractical to list summaries for each combustion; $\Delta_c U^\circ_m/M$ for all the combustion calorimetric measurements made on each of these compounds are reported in Table 5. Values of $\Delta_c U^\circ_m/M$ in Tables 3 and 5 for the C,H,O,N compounds refer to the general reaction:

$$C_aH_bO_cN_d(\text{cr or l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \quad (1)$$

Values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for 2,2′-bis(phenylthio)propane refer to the reaction

$$C_{15}H_{16}S_2(cr) + 22O_2(g) + 224H_2O(l) = 15CO_2(g) + 2(H_2SO_4{\cdot}115H_2O)\ (aq) \quad (1a)$$

As noted above, with the exception of 2,2′-bis(phenylthio)propane combustion measurements, all the values of $\Delta_c U^\circ_m/M$ refer to unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products. Corrections for the small amounts of nitric acid, formed during the combustions of the 2-aminoisobutyric acid sample, were made during the conversion to standard states (Hubbard et al., 1956) on the basis of a value of −59.7 kJ·mol^{-1} for the energy of formation of 0.1 mol·dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l).

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,N compounds refer to eq 1. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$aC(\text{cr, graphite}) + \frac{b}{2}H_2(g) + \frac{c}{2}O_2(g) + \frac{d}{2}N_2(g) = C_aH_bO_cN_d(\text{cr or l}) \quad (2)$$

Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ for 2,2′-bis(phenylthio)propane

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

	$\Delta_c U^\circ_m$/kJ·mol^{-1}	$\Delta_c H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$/kJ·mol^{-1}
A	−875.16 ± 0.34	−875.16 ± 0.34	−483.52 ± 0.36
B	−2264.13 ± 0.42	−2265.99 ± 0.42	−594.28 ± 0.48
C	−5351.47 ± 0.68	−5358.91 ± 0.68	102.34 ± 0.84
D	−4797.49 ± 0.64	−4801.21 ± 0.64	−169.53 ± 0.78
E	−3564.27 ± 0.48	−3569.23 ± 0.48	−220.98 ± 0.58
F	−3990.39 ± 0.54	−3997.82 ± 0.54	−78.22 ± 0.64
G	−9455.93 ± 1.97	−9473.25 ± 1.97	80.00 ± 2.26

[a] A = acetic acid; B = 2-aminoisobutyric acid; C = (*Z*)-5-ethylidene-2-norbornene; D = 1,2-epoxy-3-phenoxypropane; E = mesityl oxide; F = 4-methylpent-1-ene; G = 2,2′-bis(phenylthio)-propane. [b] The results listed in this table are for the liquid phase for each compound except 2-aminoisobutyric acid and 2,2′-bis-(phenylthio)propane, where they apply to the crystalline phase.

refer to eq 1a. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$15C(cr, graphite) + 8H_2(g) + 2S(cr, rhombic) = C_{15}H_{16}S_2(cr) \quad (2a)$$

Uncertainties given in Table 6 are the "uncertainty interval" (Rossini, 1956). The enthalpies of formation of CO_2(g) and H_2O(l) were taken to be −(393.51 ± 0.13) kJ·mol^{-1} and −(285.830 ± 0.042) kJ·mol^{-1}, respectively, as assigned by CODATA (Cox et al., 1989). Since solutions of the exact concentration (H_2SO_4·115H_2O) were not formed in each combustion measurement for 2,2′-bis(phenylthio)-propane, enthalpies of dilution to the standard state were estimated by interpolation (see Table 4). The values of the enthalpy of formation of $H_2SO_4 \cdot nH_2O$ were interpolated from the tables in Wagman et al. (1982) adjusted to the CODATA (Cox et al., 1989) assigned values for SO_4^{2-}(aq). The standard enthalpy of formation of H_2SO_4·115H_2O used was −(887.811 ± 0.200) kJ·mol^{-1} (Cox et al., 1989). An uncertainty interval of ±0.2 kJ·mol^{-1} was assigned to the sulfuric acid enthalpies of dilution.

Vapor-Pressure Measurements. Ebulliometric vapor-pressure measurements were made for four compounds [(*Z*)-5-ethylidene-2-norbornene, 1,2-exopy-3-phenoxypropane, mesityl oxide and 4-methylpent-1-ene]. 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. Inclined-piston vapor-pressure measurements for 2,2′-bis(phenylthio)propane are listed in Table 7. For this compound, sample decomposition prevented ebulliometric vapor pressure measurements. 2-Aminoisobutyric acid melts with decomposition at approximately 600 K, and hence, no vapor-pressure measurements were possible using the NIPER equipment. Precise ebulliometric vapor-pressure measurements for acetic acid were made by Ambrose et al. at the National Physical Laboratory, Teddington, England (Ambrose et al., 1977).

The difference between the boiling and condensation temperatures (Δ*T*) for 1,2-epoxy-3-phenoxypropane increased significantly above 525 K (see Table 7). An attempt was made to make a measurement at 169 kPa (540 K), but Δ*T* started at 0.1 K and rose rapidly to greater than 0.3 K. For the mesityl oxide sample above 435 K, a slight decomposition was indicated by a slow increase in Δ*T*. For the sulfur-containing compound, 2,2′-bis(phenylthio)propane, sample decomposition became extensive above 400 K.

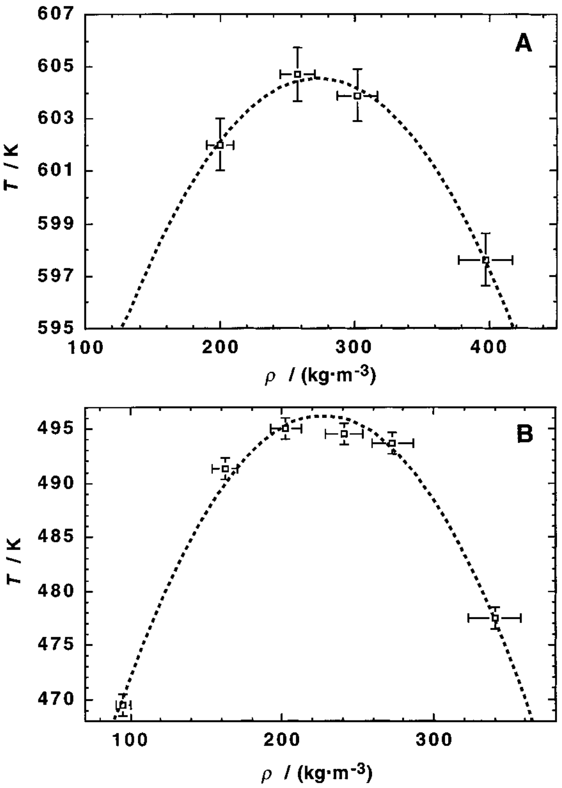

Figure 2. Vapor−liquid coexistence in the region of the critical point: A = mesityl oxide; B = 4-methylpent-1-ene. The curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty.

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 except acetic acid, for which accurate and precise adiabatic heat capacities were measured by Martin and Andon (1982). 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 or earlier sample decomposition.

For (*Z*)-5-ethylidene-2-norbornene, 1,2-epoxy-3-phenoxypropane, 2-aminoisobutyric acid, and 2,2′-bis(phenylthio)propane, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. For mesityl oxide and 4-methylpent-1-ene, measurements in the critical region were possible. For these compounds, an abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed. In each case 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 each compound. Table 9 reports the density, obtained from the mass of sample and the cell volume, V_x, calculated with eq 3

$$V_x(T)/V_x(298.15\ \mathrm{K}) = 1 + ay + by^2 \quad (3)$$

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 temperature at which conversion to a single phase was observed.

Critical temperatures and critical densities were derived graphically for mesityl oxide and 4-methylpent-1-ene with these results, as seen in Figure 2. Results of measure-

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

standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
					(*Z*)-5-Ethylidene-2-norbornene						
d	315.123	2.0022	0.0000	0.0001	0.029	w	393.825	47.385	0.001	0.002	0.005
d	329.024	4.0068	0.0000	0.0003	0.011	w	400.445	57.804	0.001	0.003	0.005
d	335.178	5.3279	0.0002	0.0003	0.011	w	407.142	70.125	0.002	0.003	0.006
d	344.420	7.9857	−0.0001	0.0005	0.008	w	413.885	84.547	0.003	0.004	0.007
d	351.403	10.6590	0.0000	0.0006	0.007	w	420.672	101.323	−0.001	0.005	0.007
d	357.051	13.329	0.000	0.001	0.006	w	427.527	120.82	0.00	0.01	0.006
d	362.953	16.686	0.000	0.001	0.005	w	434.432	143.30	−0.01	0.01	0.006
d	367.793	19.930	0.000	0.001	0.005	w	441.381	169.07	0.00	0.01	0.006
d	374.233	25.029	−0.001	0.001	0.005	w	448.382	198.54	0.00	0.01	0.007
w	374.232^b	25.030	0.001	0.001	0.005	w	455.441	232.09	0.00	0.01	0.007
w	380.715	31.187	0.000	0.002	0.004	w	462.544	270.08	0.00	0.01	0.007
w	387.242	38.572	0.001	0.002	0.004						
					1,2-Epoxy-3-phenoxypropane						
d	398.414	1.9995	−0.0001	0.0001	0.076	w	472.757	31.171	0.001	0.002	0.010
d	414.272	3.9985	0.0004	0.0002	0.038	w	480.099	38.577	0.002	0.002	0.011
d	421.383	5.3388	0.0001	0.0003	0.028	w	487.472	47.391	0.001	0.002	0.011
d	431.886	8.0034	0.0002	0.0004	0.019	w	494.888	57.838	0.003	0.003	0.013
d	439.774	10.6722	−0.0002	0.0006	0.016	w	502.349	70.140	0.001	0.003	0.014
d	446.117	13.325	−0.001	0.001	0.014	w	509.843	84.528	0.001	0.004	0.017
d	452.775	16.678	−0.001	0.001	0.011	w	517.394	101.311	−0.005	0.004	0.022
d	458.235	19.924	−0.001	0.001	0.011	w	525.004^c	120.83	0.01	0.01	0.060
d	465.492	25.030	0.000	0.001	0.010	w	532.643^c	143.27	0.00	0.01	0.077
w	465.509^b	25.044	0.001	0.001	0.011						
					Mesityl Oxide						
d	303.669	1.9935	0.0006	0.0002	0.025	w	377.804	47.341	−0.001	0.003	0.006
d	316.872	3.9936	−0.0010	0.0003	0.017	w	384.014	57.804	−0.004	0.003	0.007
d	322.781	5.3335	−0.0013	0.0003	0.016	w	390.249	70.098	−0.009	0.003	0.007
d	331.482	7.9864	−0.0011	0.0005	0.012	w	396.526	84.499	−0.011	0.004	0.008
d	338.065	10.6627	0.0001	0.0006	0.008	w	402.859	101.315	−0.014	0.005	0.009
d	343.333	13.309	0.001	0.001	0.010	w	409.229	120.80	−0.01	0.01	0.008
d	348.907	16.680	0.002	0.001	0.008	w	415.626	143.21	0.00	0.01	0.008
d	353.457	19.928	0.002	0.001	0.007	w	422.071	168.98	0.03	0.01	0.011
d	359.500	25.030	−0.002	0.001	0.005	w	428.562	198.45	0.08	0.01	0.011
w	359.483^b	25.024	0.012	0.002	0.007	w	435.083^c	231.97	0.20	0.01	0.017
w	365.557	31.177	0.007	0.002	0.006	w	441.648^c	269.98	0.35	0.01	0.021
w	371.673	38.566	0.002	0.002	0.007						
					4-Methylpent-1-ene						
w	310.360	57.827	−0.007	0.003	0.016	w	338.032	143.24	0.00	0.01	0.018
w	315.790	70.118	0.016	0.004	0.026	w	343.705	169.02	0.00	0.01	0.021
w	321.286	84.525	−0.003	0.004	0.017	w	349.419	198.46	0.01	0.01	0.026
w	326.821	101.310	−0.009	0.005	0.016	w	355.184	231.96	0.01	0.01	0.024
w	332.400	120.77	0.00	0.01	0.015	w	360.999	269.95	−0.01	0.01	0.020
					2,2′-Bis(phenylthio)propane[d]						
ip	359.977	0.0200	0.0000	0.0002		ip	384.988	0.4447	−0.0010	0.0002	
ip	364.972	0.0385	0.0000	0.0002		ip	389.968	0.7866	−0.0016	0.0003	
ip	369.974	0.0729	0.0001	0.0002		ip	392.972	1.1052	0.0011	0.0003	
ip	374.984	0.1356	0.0002	0.0002		ip	394.968^e	1.3352	−0.0420	0.0003	
ip	379.978	0.2480	0.0006	0.0002							

[a] Water (w) or decane (d) refers to which material was used as the standard in the reference ebulliometer. ip denotes inclined piston. In the ebulliometric measurements, 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 4 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 $\sigma(p) = 1.5 \times 10^{-4}p + 0.2$ Pa (inclined piston) or $\sigma(p) = (0.001)\,\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$ (ebulliometer). 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. The measurement was an overlap point between the use of decane and water as the pressure measurement standards. [c] Values at this temperature were not included in the fit of the Wagner equation due to sample decomposition, which was indicated by the increase in ΔT values (see text). [d] Due to the short temperature range of the measurements and the lack of reliable critical properties, the results were fit to eq 5 (see text). [e] The value at this temperature was not included in the fit of eq 5 because of sample decomposition.

ments on benzene and toluene performed as “proof-of-concept measurements” for these procedures have been reported (Chirico and Steele, 1994). The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl (Steele et al., 1991), dibenzothiophene (Chirico et al., 1991), and carbazole, phenanthrene, and benzofuran (Steele, 1995).

For 2,2′-bis(phenylthio)propane, which was solid 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 2,2′-bis(phenylthio)propane at the melting point 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 vaporiza-

Table 8. Heat Capacity Equations and Enthalpies of Fusion Derived from DSC Measurements ($R = 8.314\ 51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

2-Aminoisobutyric Acid (Crystalline)
$C_{\mathrm{sat,m}}/R = 4.69 + 0.0438{\cdot}T$ (in temperature range 290 K to 500 K)

(*Z*)-5-Ethylidene-2-norbornene (Liquid)
$C_{\mathrm{sat,m}}/R = 5.40 + 0.0628{\cdot}T - 2.235 \times 10^{-6}{\cdot}T^2$ (in temperature range 290 K to 440 K)

1,2-Epoxy-3-phenoxypropane (Liquid)
$C_{\mathrm{sat,m}}/R = 24.33 + 0.0217{\cdot}T + 2.531.10^{-5} \times T^2$ (in temperature range 290 K to 520 K)

Mesityl Oxide (Liquid)
$C_{\mathrm{sat,m}}/R = 17.66 + 7.507 \times 10^{-3}{\cdot}T + 4.143 \times 10^{-5}{\cdot}T^2$ (in temperature range 290 K to 580 K)

4-Methylpent-1-ene (Liquid)
$C_{\mathrm{sat,m}}/R = 29.37 - 8.819 \times 10^{-2}{\cdot}T + 2.226 \times 10^{-4}{\cdot}T^2$ (in temperature range 290 K to 460 K)

2,2′-Bis(phenylthio)propane (Crystalline)
$C_{\mathrm{sat,m}}/R = 0.56{\cdot}T - 132.00$ (in temperature range 280 K to 329 K)

2,2′-Bis(phenylthio)propane (Liquid)
$C_{\mathrm{sat,m}}/R = 26.36 + 0.072{\cdot}T$ (in temperature range 329 K to 420 K)
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$[2,2′-bis(phenylthio)propane, 329 K] = 24.4 ± 0.3 kJ mol^{-1}
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$[2,2′-bis(phenylthio)propane, 298.15 K] = 23.0 ± 0.5 kJ mol^{-1}

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

ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K
	Mesityl Oxide		
199.9	602.0	302.3	603.9
257.6	604.7	397.1	597.6
	4-Methylpent-1-ene		
95.4	469.5	241.0	494.5
162.5	491.3	272.7	493.7
202.7	495.0	340.0	477.5

Table 10. Parameters for Wagner Equation, Critical Constants, and Acentric Factors

(*Z*)-5-Ethylidene-2-norbornene		1,2-Epoxy-3-phenoxypropane	
A	−7.703 99	A	−10.713 50
B	2.103 70	B	6.254 40
C	−2.933 54	C	−8.007 63
D	−3.463 96	D	−2.911 54
T_c = 629 K	p_c = 3400 kPa	T_c = 720 K	p_c = 2950 kPa
ρ_c = 294.5 kg·m^{-3}	ω = 0.3144	ρ_c = 324 kg·m^{-3}	ω = 0.6057
4-Methylpent-1-ene		4-Methylpent-1-ene	
A	−8.681 18	A	−7.718 98
B	3.992 03	B	2.837 83
C	−4.816 62	C	−3.473 10
D	−1.731 64	D	−0.804 95
T_c = 605 K	p_c = 4000 kPa	T_c = 495 K	p_c = 3290 kPa
ρ_c = 277.7 kg·m^{-3}	ω = 0.3587	ρ_c = 238 kg·m^{-3}	ω = 0.2548

tion for each compound (except acetic acid and 2-aminoisobutyric acid) over as wide a temperature range as possible. Although $\Delta_{\mathrm{g}}^{\mathrm{l}}H_{\mathrm{m}}$ at 298.15 K is the only value necessary to obtain $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$(g,298.15 K), the benefit of a 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 (Steele, 1995).

With the exception of 2,2′-bis(phenylthio)propane, the fitting parameters were derived by a nonlinear least-squares fit of the vapor pressures listed in Table 7 using the Wagner equation (Wagner, 1973) in the formulation given by Ambrose and Walton (1989)

$$\ln(p/p_c) = (1/T_r)\,[AY + BY^{1.5} + CY^{2.5} + DY^5] \qquad (4)$$

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 Steele (1995). The number of fitting parameters differed depending on whether or not a critical temperature could be determined experimentally. For (*Z*)-5-ethylidene-2-norbornene and 1,2-epoxy-3-phenoxypropane, extensive sample decomposition precluded critical temperature measurements and, therefore, both T_c and p_c were included as variables. For mesityl oxide and 4-methylpent-1-ene, critical temperatures were determined from the DSC measurements and, hence, only the critical pressure p_c was included in the variables. Deviations of the experimental values from the fits are given in Table 7.

For 2,2′-bis(phenylthio)propane, which decomposed well below the critical region, and the measured vapor pressures covering a relatively narrow range of temperature (Table 7), all estimating procedures gave unrealistic values for the critical pressure. A simplified form of the vapor-pressure equation

$$\ln(p/p_{\mathrm{ref}}) = 43.8413 - 17\ 189.5/(T/\mathrm{K}) \qquad (5)$$

with $p_{\mathrm{ref}} = 1$ kPa, was fit to the vapor-pressure measurements. Details of the fit to the vapor-pressure results are given in Table 7.

Enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (Table 10) were derived from the Wagner-equation fits using the Clapeyron equation

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}/(T\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}) \qquad (6)$$

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_{m}(l), were made with the extended corresponding-states equation (Riedel, 1954) as formulated by Hales and Townsend (1972)

$$(\rho/\rho_c) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)\,Y^{1/3} \qquad (7)$$

with $Y = (1 - T/T_c)$, ρ_c = critical density, and ω = acentric factor. The acentric factor, ω, is defined as $[-\log(p/p_c) - 1]$, where p is the vapor pressure at $T/T_c = 0.7$ and p_c is 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 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 (Pitzer and Curl, 1957), and third virial coefficients were estimated with the corresponding-states method (Orbey and Vera, 1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene (Chirico and Steele, 1994). 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

Table 11. 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}
	(Z)-5-Ethylidene-2-norbornene		
298.15[b]	44.39 ± 0.30	420.0	36.63 ± 0.38
300.0[b]	44.27 ± 0.30	440.0	35.21 ± 0.48
320.0	42.99 ± 0.27	460.0	33.71 ± 0.62
340.0	41.74 ± 0.25	480.0[b]	32.09 ± 0.78
360.0	40.50 ± 0.25	500.0[b]	30.33 ± 0.96
380.0	39.25 ± 0.27	520.0[b]	28.4 ± 1.2
400.0	37.96 ± 0.30		
	1,2-Epoxy-3-phenoxypropane		
298.15[b]	69.85 ± 0.72	460.0	54.93 ± 0.40
340.0[b]	65.80 ± 0.58	480.0	53.11 ± 0.43
360.0[b]	63.93 ± 0.55	500.0	51.26 ± 0.50
380.0[b]	62.09 ± 0.50	520.0	49.35 ± 0.60
400.0	60.29 ± 0.47	540.0[b]	47.40 ± 0.75
420.0	58.50 ± 0.43	560.0[b]	45.37 ± 0.91
440.0	56.72 ± 0.42	580.0[b]	43.3 ± 1.1
	Mesityl Oxide		
260.0[b]	44.90 ± 0.33	380.0	37.79 ± 0.28
280.0[b]	43.73 ± 0.30	400.0	36.45 ± 0.33
298.15[b]	42.70 ± 0.28	420.0	35.03 ± 0.43
300.0[b]	42.59 ± 0.28	440.0	33.52 ± 0.57
320.0	41.43 ± 0.27	460.0[b]	31.91 ± 0.72
340.0	40.26 ± 0.25	480.0[b]	30.18 ± 0.90
360.0	39.05 ± 0.25	500.0[b]	28.3 ± 1.1
	4-Methylpent-1-ene		
280.0[b]	29.43 ± 0.18	360.0	24.91 ± 0.48
298.15[b]	28.57 ± 0.20	380.0[b]	23.44 ± 0.63
300.0[b]	28.48 ± 0.20	400.0[b]	21.81 ± 0.80
320.0	27.42 ± 0.25	420.0[b]	20.0 ± 1.0
340.0	26.24 ± 0.35		

[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.

vaporization are reported in Table 11. For $p > 1$ bar, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

For 2,2′-bis(phenylthio)propane, a value $\Delta_l^g H_m(376\ \mathrm{K}) = 143$ kJ·mol^{-1} was derived using eqs 5 and 6. A corresponding value at 298.15 K $\Delta_l^g H_m(298.15\ \mathrm{K}) = 159$ kJ·mol^{-1} was obtained using Watson's empirical equation (Watson, 1931). A critical temperature of 610 K was estimated (Joback, 1984) for use in Watson's equation.

Ideal-Gas Enthalpies of Formation. Table 12 summarizes the thermochemical property measurements and derived ideal-gas standard enthalpies of formation for all the compounds of this study. The enthalpy of vaporization, $\Delta_l^g H_m$, for 4-methylpent-1-ene was converted to the corresponding value for the ideal gas, $\Delta_l^g H_m^\circ$ using an estimate, $(H^\circ - H) = 0.21$ kJ·mol^{-1}, for the real gas at its saturation vapor pressure at 298.15 K. The estimate was calculated using eq 20 of Chirico et al. (1993) and virial coefficients derived as described above. The corresponding corrections for the remaining compounds, which are less volatile, were calculated to be negligibly small.

Discussion

Acetic Acid. The standard energy of combustion of acetic acid has been measured six times previously. As stated by both Sunner and Wadsö (1957) and Evans and Skinner (1959), the early measurements from the 19th century are of historic interest only. Evans and Skinner (1959) measured the energy of combustion of acetic acid on a sample whose exact purity was not noted. Also, they listed only four combustions, for which three gave small amounts of unburned carbon. The energy of combustion listed by Evans and Skinner (1959) was $(\Delta_c U_m^\circ/M(C_2H_4O_2$, l, 298.15 K$) = -(14.5631 \pm 0.0015)$ kJ·g^{-1}. Lebedeva (1964) measured the energies of combustion of 12 monocarboxylic acids, including acetic acid. Lebedeva lists a sample purity of 99.8 mol % stating that "most of the acids could not be improved by further purification." Lebedeva also states that "analysis of the gaseous products gave a carbon content not less than 99.97% of theoretical, which suggests that the impurities are isomeric compounds." Lebedeva lists $\Delta_c U_m^\circ/M = -(14.5703 \pm 0.0038)$ kJ·g^{-1}. Although the agreement between both sets of measurements is excellent, continued questions by DIPPR 871 Committee members on the reliability of the results led to the present measurements. In the present measurements, the energy of combustion reported refers to unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion. The value $\Delta_c U_m^\circ/M = -(14.5731 \pm 0.0017)$ kJ·g^{-1} (Table 5) obtained is in near perfect agreement with that obtained by Lebedeva. A weighted mean of all three combustion calorimetric studies gives $\Delta_f U_m^\circ(C_2H_4O_2$, l, 298.15 K$) = -(483.8 \pm 0.4)$ kJ·mol^{-1}.

Determination of the ideal-gas enthalpy of formation of acetic acid requires the corresponding enthalpy of vaporization at 298.15 K, $\Delta_l^g H_m(C_2H_4O_2$, 298.15 K). Compilations of thermochemical data (Majer and Svoboda, 1985; Pedley et al., 1986; Pedley, 1994) all list $\Delta_l^g H_m(C_2H_4O_2$, 298.15 K$) = (51.6 \pm 1.5)$ kJ·mol^{-1}. This value derives from the measurements of Konicek and Wadsö (1970). A comprehensive review of the available literature to update the Konicek and Wadsö value was beyond the scope of this research. Further detailed studies of the vaporization of acetic acid, as an extension of the work by Jasperson et al. (1989) on formic, C_3 through C_6 *n*-acids, acrylic, and methacrylic acids, in the DIPPR 832 Project, would appear to be in order.

2-Aminoisobutyric Acid. Adkins and Billca (1948) noted that 2-aminoisobutyric acid decomposes explosively when heated rapidly. In this research, samples of the acid were never heated rapidly or to temperatures above 520 K. Svec and Clyde (1965) measured vapor pressures for 13 α-amino acids by the Knudsen cell effusion method. They list an enthalpy of sublimation of 2-aminoisobutyric acid $\Delta_{cr}^g H_m(C_4H_9O_2N$, 455 K$) = (125.9 \pm 0.4)$ kJ·mol.$^{-1}$ [The constants listed in Table II Svec and Clyde (1965) are in error. The values of B listed should be 3.00 less than those quoted, if the pressures listed in Table I of Svec and Clyde (1965) are to be reproduced.] Using Sidwick's rule (Cox and Pilcher, 1970), an enthalpy of sublimation $\Delta_{cr}^g H_m(C_4H_9O_2N$, 298.15 K$) = (135 \pm 5)$ kJ·mol^{-1} is estimated. Using the enthalpy of formation for crystalline 2-aminoisobutyric acid obtained in this research, $\Delta_f H_m^\circ(C_4H_9O_2N$, cr, 298.15 K$) = -(594.28 \pm 0.48)$ kJ·mol^{-1}, (Tables 6 and 12), a standard ideal-gas enthalpy of formation, $(\Delta_f H_m^\circ(C_4H_9O_2N$, g, 298.15 K$) = -(459 \pm 5)$ kJ·mol^{-1}, is derived.

Using the group parameters given in Benson (1976), Reid et al. (1987), and Eigenmann et al. (1973)

2	C−(C)(H)$_3$	−42.20	−84.40
1	N−(C)(H)$_2$	20.1	20.1
1	(CO)−(O)(C)	−146.96	−146.96
1	O−(CO)(H)	−243.25	−243.25
1	C−(N)(C)$_2$(CO)	?.?	−?.?

$$\Delta_f H_m^\circ(C_4H_9O_2N,\ g,\ 298.15\ \mathrm{K}) = -(459 \pm 5)\ \mathrm{kJ{\cdot}mol^{-1}}$$

Hence, the C-(N)(C)$_2$(CO) group-additivity parameter equals −4.5 kJ·mol^{-1}.

(Z)-5-Ethylidene-2-norbornene. 5-Ethylidene-2-norbornene exists as two isomers, *cis*- and *trans*-, and the

Table 12. Thermochemical Properties at 298.15 K (R = 8.314 51 J·K^{-1}·mol^{-1} and $p°$ = 101.325 kPa)[a]

	$\Delta_f H^\circ_m$(c)/kJ·mol^{-1}	$\Delta^{l}_{cr}H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$(l)/kJ·mol^{-1}	$\Delta^{g}_{l}H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$(g)/kJ·mol^{-1}
A			−483.52 ± 0.36		
B	−594.28 ± 0.48				
C			102.34 ± 0.84	44.39 ± 0.30	146.73 ± 0.89
D			−169.53 ± 0.78	69.85 ± 0.72	−99.68 ± 1.06
E			−220.98 ± 0.58	42.70 ± 0.28	−178.28 ± 0.64
F			−78.22 ± 0.64	28.78 ± 0.20[b]	−49.44 ± 0.67
G	80.00 ± 2.26	23.0 ± 0.5	103.0 ± 2.3	159 ± 10	262.0 ± 10.3

[a] A = acetic acid; B = 2-aminoisobutyric acid; C = (Z)-5-ethylidene-2-norbornene; D = 1,2-epoxy-3-phenoxypropane; E = mesityl oxide; F = 4-methylpent-1-ene; G = 2,2′-bis(phenylthio)propane. [b] Vapor pressure is 36.4 kPa at 298.15 K. Gas imperfection correction required as an addition to the value listed in Table 11.

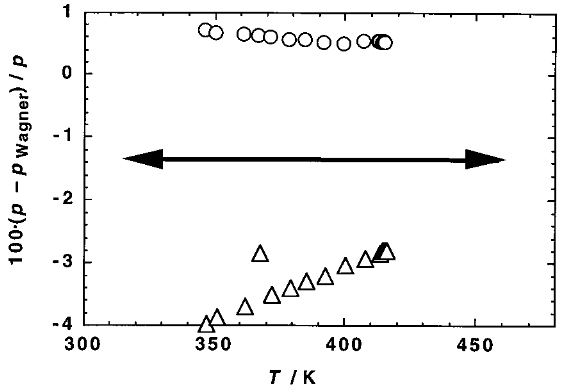

Figure 3. Comparison of literature vapor pressures for 5-ethylidene-2-norbornene with values obtained using the Wagner equation (eq 4) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor-pressure measurements for the (Z)-isomer obtained in this research (Table 7). (○) Varushchenko et al. (1973), (Z)-isomer. (△) Varushchenko et al. (1973), (E)-isomer.

sample obtained from Aldrich contained both isomers (as shown by CGC analysis) in an approximate ratio of 100 to 1. Subsequent repeated spinning-band distillations removed the isomer present in the smaller concentration. Proton NMR analysis showed the purified compound to be *cis*-5-ethylidiene-2-norbornene (i.e., (Z)-5-ethylidiene-2-norbornene).

Pedley (Pedley et al., 1986; Pedley, 1994) in his texts on thermochemical data lists a series of measurements on (Z)-5-ethylidiene-2-norbornene, CA number (28304-66-7), made by Kozina et al. (1971). Kozina et al. defined their compound as the "low-boiling isomer in which the methyl group is *cis*- in relation to the CH_2 group of the ring"). Kozina et al. list an enthalpy of combustion $\Delta_c H^\circ_m$[(Z)-C_9H_{12}, l, 298.15 K] = −(5358.78 ± 1.59) kJ·mol^{-1} in near perfect agreement with the value $\Delta_c H^\circ_m$ = −(5358.91 ± 0.68) kJ·mol^{-1} obtained in this research. In a subsequent publication, Kozina et al. (1972) listed an enthalpy of combustion for the *trans*-isomer $\Delta_c H^\circ_m$[(E)-C_9H_{12}, l, 298.15 K] = −(5363.13 ± 1.76) kJ·mol^{-1}.

Varushchenko et al. (1973, 1974) measured ebulliometrically the vapor pressures of both (Z)- and (E)-5-ethylidene-2-norbornene. The full results were obtained from the VINITI deposited document (Varushchenko et al., 1973). Varushchenko et al. (1974) reports only the normal boiling points and enthalpies of vaporization at 298.15 K. The *trans*-isomer used by Varushchenko et al. contained 6.8% of the *cis*-isomer. Figure 3 compares the results of the Varushchenko et al. (1973) ebulliometric measurements with values obtained using the Wagner vapor-pressure equation and the parameters listed in Table 10. Varushchenko et al. (1973) list differences between the boiling and condensation temperatures for their measurements on the *cis*-isomer (0.028 K at 360.9 K, 0.044 K at 391.6 K, and 0.042 K at 415.1 K). In the measurements reported here, the average difference between the boiling and condensation temperatures was only 6 mK over most of the temperature range (see Table 7). The obvious difference between the relative purities of the *cis*-isomer samples studied in the vapor pressure measurements probably accounts for the 0.005·p difference shown in Figure 3. The enthalpy of vaporization $H^{g}_{l}H_m$[(Z)-C_9H_{12}, 298.15 K] = (43.51 ± 0.67) kJ·mol^{-1} listed by Varushchenko et al. (1973, 1974) compares with the value $\Delta^{g}_{l}H_m$[(Z)-C_9H_{12}, 298.15 K] = (44.39 ± 0.30) kJ·mol^{-1} obtained in this research. Varushchenko et al. (1977) developed a precision enthalpy of the vaporization calorimeter. Measurements on the *cis*-isomer gave a value $\Delta^{g}_{l}H_m$[(Z)-C_9H_{12}, 298.15 K] =(44.14 ± 0.14) kJ·mol^{-1}. Subsequently Druzhinina and Varushchenko (1978) derived a value $\Delta^{g}_{l}H_m$[(Z)-C_9H_{12}, 298.15 K] = (44.52 ± 0.54) kJ·mol^{-1} using their earlier vapor-pressure measurements. Agreement of these latter two results with the value listed in Table 11 is excellent.

Estimation of the ideal-gas enthalpies of formation of both the *cis*- and *trans*-isomers of 5-ethylidene-2-norbornene follows. Using the group parameters given in (Benson, 1976; Reid et al., 1987), the *cis* interaction term derived in the 1988 Project 871 measurements (Steele et al., 1990), and the strain energy for the bicyclo[2.2.1]hept-2-ene ring system (Steele et al., 1996c)

1	C−(C)$_2$(H)$_2$	−20.72	−20.72
1	C−(C$_d$)(C)(H)$_2$	−19.93	−19.93
1	C−(C$_d$)(C)$_2$(H)	−6.20	−6.20
1	C−(C$_d$)$_2$(C)(H)	−5.19	−5.19
3	C$_d$−(C$_d$)(C)(H)	35.96	107.88
1	C$_d$−(C$_d$)(C)$_2$	43.29	43.29
1	C−(C$_d$)(H)$_3$	−42.20	−42.20
1	bicyclo[2.2.1]hept-2-ene ring strain	84.9	84.9
1	olefin *cis* interaction term	4.0	4.0

$$\Delta_f H^\circ_m[(Z)\text{-}C_9H_{12},\ g,\ 298.15\ K] = 145.8\ kJ\cdot mol^{-1}$$

This compares with the value $\Delta_f H^\circ_m$[(Z)-C_9H_{12}, g, 298.15 K] = (146.73 ± 0.89) kJ·mol^{-1} obtained in this research (see Table 12).

1	C−(C)$_2$(H)$_2$	−20.72	−20.72
1	C−(C$_d$)(C)(H)$_2$	−19.93	−19.93
1	C−(C$_d$)(C)$_2$(H)	−6.20	−6.20
1	C−(C$_d$)$_2$(C)(H)	−5.19	−5.19
3	C$_d$−(C$_d$)(C)(H)	35.96	107.88
1	C$_d$−(C$_d$)(C)$_2$	43.29	43.29
1	C−(C$_d$)(H)$_3$	−42.20	−42.20
1	bicyclo[2.2.1]hept−2−ene ring strain	84.9	84.9

$$\Delta_f H^\circ_m[(E)\text{-}C_9H_{12},\ g,\ 298.15\ K] = (141.8)\ kJ\cdot mol^{-1}$$

This derived value is in stark contrast to the value $\Delta_f H^\circ_m$[(E)-C_9H_{12}, g, 298.15 K] = (150.4 ± 2.0) kJ·mol^{-1} obtained by Kozina et al. (1972). The results given by Kozina et al. (1972) make the *trans*-isomer *less* stable than the *cis*-isomer.

1,2-Epoxy-3-phenoxypropane (Glycidyl Phenyl Ether). Other than approximately a dozen single-temperature density measurements and approximately 40 boiling-point determinations found in a Beilstein search through January 1997, the only other thermochemical or thermophysical property measurements found for 1,2-epoxy-3-phenoxypropane were measurements of heat capacities (Lebedev et al., 1988) and the energy of combustion (Küznetsova et al., 1976). The energy of combustion was not abstracted by Pedley in either of his recent thermochemical data compilations (Pedley et al., 1986; Pedley, 1994).

Agreement between the heat capacities $C_{\mathrm{sat,m}}$ obtained in this research (Table 8) with those listed in Lebedev et al. (1988) is excellent although the sample was only 99.3 mol% pure. Küznetsova et al. (1976) measured the energy of combustion of 1,2-epoxy-3-phenoxypropane [a possible minimum of five combustions with results based on CO_2 analyses (accurate to ±0.05%)]. They do not list a purity for the glycidyl phenyl ether but do make the general statement, "content of impurities no more than 0.1 to 0.2%," when speaking of both the glycidyl phenyl ether and the amines used in the study. The listed enthalpy of combustion $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(C_9H_{10}O_2, \mathrm{l}, 298.15\ \mathrm{K}) = -(4784.8 \pm 0.2)\ \mathrm{kJ{\cdot}mol^{-1}}$ is in very poor agreement with the value $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(C_9H_{10}O_2, \mathrm{l}, 298.15\ \mathrm{K}) = -(4801.2 \pm 0.6)\ \mathrm{kJ{\cdot}mol^{-1}}$ obtained in this research (Table 6). Küznetsova et al. (1976) measured the enthalpy of vaporization at 298.15 K of 1,2-epoxy-3-phenoxypropane "directly using a Calvet-type calorimeter." Their result, $[\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}C_9H_{10}O_2, 298.15\ \mathrm{K}] = (65.61 \pm 0.08)\ \mathrm{kJ{\cdot}mol^{-1}}$, is also in poor agreement with the value, $[\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}C_9H_{10}O_2, 298.15\ \mathrm{K}] = (69.85 \pm 0.72)\ \mathrm{kJ{\cdot}mol^{-1}}$, obtained in this research (Table 11).

Estimation of the ideal-gas enthalpy of formation of 1,2-epoxy-3-phenoxypropane (glycidyl phenyl ether) follows. Using the group parameters given in Benson (1976) and Reid et al. (1987) and, where noted, unpublished NIPER derived values

5	C_b-$(C_b)_2$(H)	13.82	69.10	
1	C_b−$(C_b)_2$(O)	1.6	1.6	NIPER
1	O−(C_b)(C)	−96.20	−96.20	NIPER
2	C−(O)(C)$(H)_2$	−33.91	−67.82	
1	C−(O)$(C)_2$(H)	−30.14	−30.14	
1	O−$(C)_2$	−97.07	−97.07	NIPER
1	ring strain energy	112.3	112.3	

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(C_9H_{10}O_2, \mathrm{g}, 298.15\ \mathrm{K}) = -108.2\ \mathrm{kJ{\cdot}mol^{-1}}$$

This compares with the value $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(C_9H_{10}O_2, \mathrm{g}, 298.15\ \mathrm{K}) = -(99.68 \pm 1.06)\ \mathrm{kJ{\cdot}mol^{-1}}$ obtained in this research (Table 12). The difference between the value calculated using the group additivity parameters and that measured in this research, 8 kJ·mol^{-1}, is twice that usually obtained (±4 kJ·mol^{-1}). As noted in the 1992 Project 871 Report (Steele et al., 1996c), further work on aliphatic and aromatic ethers is required to reconcile the various sets of group parameters.

Mesityl Oxide (4-Methyl-3-penten-2-one). CGC analyses showed the sample of mesityl oxide (i.e., 4-methyl-3-penten-2-one) obtained from Aldrich contained approximately 16% of isomesityl oxide (4-methyl-4-penten-2-one). Several spinning-band distillations resulted in a calorimetric sample for which CGC analyses failed to show the presence of any iso oxide. Further details of measurements of the tautomerism of mesityl oxide are given in Hesse et al. (1967).

A search of the literature found a number of references to thermochemical and thermophysical property measurements on mesityl oxide. The following section compares the literature data with values obtained in this research.

All literature references to the critical properties of mesityl oxide were estimates. Values of the critical temperature estimated ranged from 600 K (Stross et al., 1947; Daubert et al., 1994) to 605 K (Yerlett and Wormald, 1986) with corresponding critical pressures of 3550 kPa, 3410 kPa, and 4950 kPa. At NIPER, the DSC measurements and fitting procedures gave $T_{\mathrm{c}} = (605 \pm 1)$ K with $\rho_{\mathrm{c}} = (278 \pm 10)\ \mathrm{kg{\cdot}m^{-3}}$ and $p_{\mathrm{c}} = (4000 \pm 100)$ kPa.

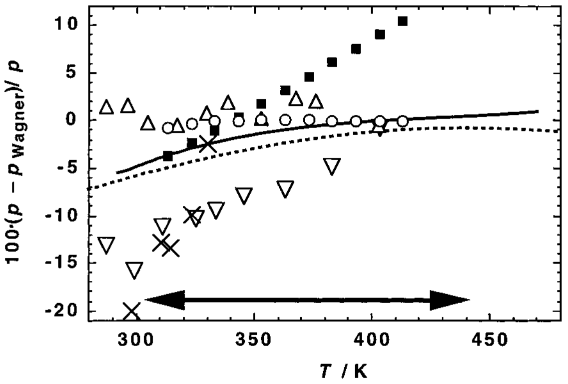

Figure 4. Comparison of literature vapor pressures for mesityl oxide with values obtained using the Wagner equation (eq 4) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor pressure measurements obtained in this research (Table 7). The solid line represents the equation listed by Ambrose et al. (1975). The dashed line represents the DIPPR Project 801 correlation equation (Daubert et al., 1994). Key: (×) Kahlbaum, (1885); (○) Stross et al. (1947); (▽) Stull (1947); (△) Fuge et al. (1952); (■) Mozgovaya et al. (1978).

Figure 4 compares sets of vapor-pressure measurements on mesityl oxide reported in the literature (Kahlbaum, 1885; Stross et al., 1947; Stull, 1947; Fuge et al., 1952; Ambrose et al., 1975; Mozgovaya et al., 1978; Daubert et al., 1994) with values obtained using the Wagner equation and the parameters listed in Table 10. Stull (1947) probably used the results of Kahlbaum (1885) in his compilation. The results of Stross et al. (1947) and Fuge et al. (1952) are in good agreement with vapor pressures measured in this research. Ambrose et al. (1975) estimated a vapor pressure equation for mesityl oxide after deriving a correlation for saturated aliphatic ketones. Mozgovaya et al. (1978) deposited their results at the All-Union Institute Of Scientific And Technical Information (VINITI), but full documentation could not be obtained by the authors of the present paper. The DIPPR Project 801 correlation equation (Daubert et al., 1994) gives vapor pressures that replicate Stross et al. (1947) and Fuge et al. (1952) across the whole region shown in Figure 4.

Figure 5 compares literature values for the density of mesityl oxide (Perkins, 1888; Getman, 1910; Stross et al., 1947; Fuge et al., 1952; Daubert et al., 1994) with values calculated using extended corresponding states (eq 7) and the parameters listed in Table 10. The density obtained (Table 2) from measurements of volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, 850 kg·m^{-3} at 298.15 K, was used to determine ρ_{c} and, consequently, matches exactly that derived using eq 7. The DIPPR Project 801 correlation equation (Daubert et al., 1994) gives heavy weight to the measurements of Fuge et al. (1952).

Table 13 compares literature enthalpies of vaporization (Louguinine, 1898; Stross et al., 1947; Fuge et al., 1952; Ambrose et al., 1975) with values obtained in this research (Table 11). Agreement is within the probable uncertainty limits.

Measurements of the energy of combustion (Lebedeva et al., 1975) were not abstracted by Pedley in either of his recent thermochemical data compilations (Pedley et al., 1986; Pedley, 1994). Lebedeva et al. (1975) also measured energies of combustion for methacrylic acid, *N*,*N*-diethyl-

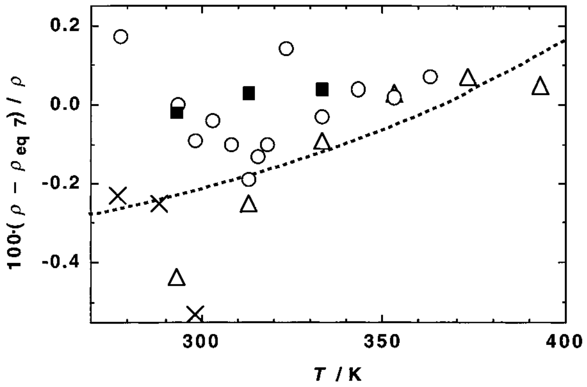

Figure 5. Comparison of literature saturation densities for mesityl oxide with values obtained by extended corresponding states, eq 7, and the parameters given in Table 10. The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (×) Perkins (1888); (○) Getman (1910); (■) Stross et al. (1947); (△) Fuge et al. (1952).

Table 13. Comparison of Enthalpies of Vaporization Found in a Search of the Literature with Values Derived in This Research

reference	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	Δ/kJ·mol^{-1} [a]
	Mesityl Oxide		
Louguinine (1898)	35.22	401.5	−1.12
Stross et al. (1947)	45.81	273.15	1.68
	41.25	327.58	0.26
	40.29	343.38	0.23
	36.11	402.89	−0.14
Fuge et al. (1952)	43.28	293.14	0.30
	36.96	402.93	0.71
Ambrose et al. (1975)	43.40	298.15	0.70
	36.40	402.9	0.15
	4-Methylpent-1-ene		
Camin and Rossini (1956)	28.70	298.135	0.13
	27.07	326.992	0.05

[a] $\Delta = \Delta_l^g H_m(\text{ref}) - \Delta_l^g H_m(\text{this research})$ in units of kJ·mol^{-1}.

2-methyl-2-propen-1-amine, and methacrylamide. The enthalpy of combustion for mesityl oxide $\Delta_c H_m^\circ(C_6H_{10}O, \text{l}, 298.15\ \text{K}) = -(3571.04 \pm 0.84)$ kJ·mol^{-1} given by Lebedeva et al. is in good agreement with the value $\Delta_c H_m^\circ(C_6H_{10}O, \text{l}, 298.15\ \text{K}) = -(3569.23 \pm 0.48)$ kJ·mol^{-1} obtained in this research (Table 6).

Estimation of the ideal-gas enthalpy of formation of mesityl oxide follows. Using the group parameters given in Benson (1976) and Reid et al. (1987) and the $C_d-(CO)(C_d)(H)$ group value given by Eigenmann et al. (1973)

2	$C-(C_d)(H)_3$	−42.20	−84.40
1	$C-(CO)(H)_3$	−42.20	−42.20
1	$C_d-(C_d)(C)_2$	43.29	43.29
1	$C_d-(CO)(C_d)(H)$	20.9	20.9
1	$(CO)-(C_d)(C)$	?.?	?.?

$$\Delta_f H_m^\circ(C_6H_{10}O, \text{g}, 298.15\ \text{K}) = -(178.28 \pm 0.64)\ \text{kJ·mol}^{-1}$$

Hence the $(CO)-(C_d)(C)$ group-additivity parameter equals −115.9 kJ·mol^{-1}.

Reid et al. (1987) list a value of 35.59 kJ·mol^{-1} for the $C_d-(CO)(C_d)(H)$ group. If that value is used in the above calculation, then the $(CO)-(C_d)(C)$ group-additivity parameter equals -130.6 kJ·mol^{-1}. In the 1992 Project 871 Report (Steele et al., 1996c), a value of −104.0 kJ·mol^{-1} was obtained for the sum of the $(CO)-(C_d)(O)$ and $C_d-(CO)(C_d)(H)$ groups. In this research, the sum of the $(CO)-(C_d)(C)$ and $C_d-(CO)(C_d)(H)$ groups is −95.0 kJ·mol^{-1}. Additional enthalpy of formation measurements on compounds that contain one, but not both, groups would be beneficial in resolving the discrepancies that still exist. Until then, calculations using these group-additivity parameters should be undertaken with care.

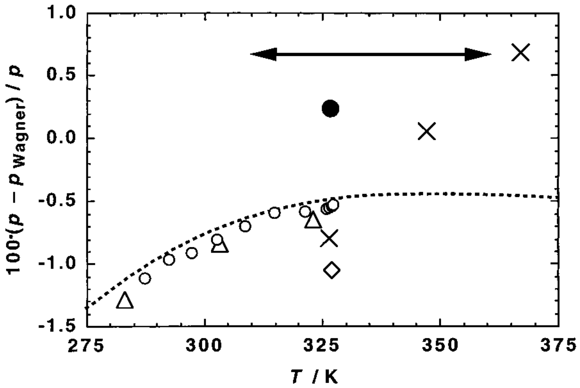

Figure 6. Comparison of literature vapor pressures for 4-methylpent-1-ene with values obtained using the Wagner equation (eq 4) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (Table 7). The dashed line represents the DIPPR Project 801 correlation equation (Daubert et al., 1994). Key: (●) Schmitt and Boord (1932); (◇) Boord et al. (1949); (○) Camin and Rossini (1956); (×) Martire and Pollara (1965); (△) Vera and Prausnitz (1971).

4-Methylpent-1-ene. A search of the literature found a number of references to thermochemical and thermophysical property measurements on 4-methylpent-1-ene. The following section compares the literature values with those obtained in this research.

All critical properties of 4-methylpent-1-ene found in the literature search were estimates. Estimated values of the critical temperature ranged from 493.3 K (Vera and Prausnitz, 1971) to 495 K (Steele and Chirico, 1993) with corresponding critical pressures of 3220 kPa and 3290 kPa. The DSC measurements and fitting procedures of this research gave $T_c = (495 \pm 1)$ K with $\rho_c = (238 \pm 10)$ kg·m^{-3} and $p_c = (3290 \pm 100)$ kPa.

Figure 6 compares sets of vapor pressure measurements on 4-methylpent-1-ene reported in the literature (Schmitt and Boord, 1932; Boord et al., 1949; Camin and Rossini, 1956; Martire and Pollara, 1965; Vera and Prausnitz, 1971; Daubert et al., 1994) with values obtained using the Wagner equation and the parameters listed in Table 10. Agreement between the measurements is relatively poor. Usually the agreement between measurements made at Bartlesville and those of Rossini's group is within a few tenths of 1%, but not in this case. Camin and Rossini (1956) note that their sample was (99.85 ± 0.13) mol % pure. The sample used in this research was analyzed by CGC using both a polar and a nonpolar column and was shown to be >99.95 mol % pure. This purity difference does not seem large enough to be the source of all the discrepancy. The DIPPR Project 801 correlation equation (Daubert et al., 1994) gives heavy weight to the measurements of Camin and Rossini (1956).

Values for the density of 4-methylpent-1-ene were compiled as part of the review on alkenes made by Steele and Chirico (1993) [see Table 3 of Steele and Chirico (1993)]. As noted in that table, agreement between the majority of the measurements is excellent (although the temperature range is short, 293.15 K to 347.6 K). The DIPPR Project 801 correlation equation (Daubert et al., 1994) deviates from the measurements reported in Steele and Chirico (1993) by 0.5% at 347.6 K. The correlation should be checked.

Bartolo and Rossini (1960) reported the energies of combustion of the 17 isomeric hexenes, but published their results relative to the value obtained for hex-1-ene for which they did not state an absolute value. Steele and Chirico (1993), using Bartolo's thesis (Bartolo, 1956), listed absolute enthalpies of formation for all 17 isomeric hexenes. As per Table 7 of Steele and Chirico (1993), the enthalpy of combustion for 4-methylpent-1-ene $\Delta_c H^\circ_m(C_6H_{12}, l, 298.15\ K) = -(3998.06 \pm 1.76)\ kJ\cdot mol^{-1}$ is in near-perfect agreement with the value $\Delta_c H^\circ_m(C_6H_{12}, l, 298.15\ K) = -(3997.82 \pm 0.54)\ kJ\cdot mol^{-1}$ obtained in this research (Table 6).

Camin and Rossini (1956) derived enthalpies of vaporization at 298.15 K and the normal boiling point from their vapor pressure studies and the Clapeyron equation for each of the 17 isomeric hexenes. Their results for 4-methylpent-1-ene are compared in Table 13 with values obtained in this research. Agreement is good regardless of the discrepancies in the vapor-pressure measurements (see above).

Estimation of the ideal-gas enthalpy of formation of 4-methylpent-1-ene follows. Using the group parameters given in Table 14 of Steele et al. (1990)

1	$C_d-(C_d)(H)_2$	26.21	26.21
1	$C_d-(C_d)(C)(H)$	35.96	35.96
1	$C-(C_d)(C)(H)_2$	−19.93	−19.93
1	$C-(C)_3(H)$	−7.95	−7.95
2	$(C)-(C)(H)_3$	−42.20	−84.40

$$\Delta_f H^\circ_m(C_6H_{12}, g, 298.15\ K) = -50.11\ kJ\cdot mol^{-1}$$

The value is in excellent agreement with the value, $\Delta_f H^\circ_m C_6H_{12}, g, 298.15\ K) = -(49.44 \pm 0.67)\ kJ\cdot mol^{-1}$, obtained in this research (Table 12). The group parameters listed in Table 14 of Steele et al. (1990) are now well established [see also Table 12 and section 5.2 of Steele and Chirico (1993)].

2,2′-Bis(phenylthio)propane. A search of the literature found only a single reference, Schoenberg and Praefcke (1967), to either thermochemical or thermophysical property measurements for 2,2′-bis(phenylthio)propane. The listed boiling point, 419 K at 0.013 kPa (Schoenberg and Praefcke, 1967), is in complete disagreement (by at least a factor of 10 on the pressure scale) with the results of the inclined-piston measurements given in Table 7.

Using the group parameters given in Benson (1976) and Reid et al. (1987)

10	$C_b-(C_b)_2(H)$	13.82	138.2
2	$C_b-(C_b)_2(S)$	−7.5	−15.0
2	$S-(C_b)(C)$	80.22	160.44
2	$C-(C)(H)_3$	−42.20	−84.40
1	$C-(S)_2(C)_2$	?.?	−?.?

$$\Delta_f H^\circ_m(C_{15}H_{16}S_2, g, 298.15\ K) = (262.0 \pm 10.3)\ kJ\cdot mol^{-1}$$

Hence, the $C-(S)_2(C)_2$ group-additivity parameter equals 63 kJ·mol^{-1}.

Conclusions

Confirmation of Literature Enthalpies of Formation, Revised or New Groups, Ring-Strain Energies, and Interaction Terms. The enthalpy of formation of acetic acid in the liquid phase was confirmed as $\Delta_f H^\circ_m(CH_3COOH, l, 298.15\ K) = -(483.8 \pm 0.4)\ kJ\cdot mol^{-1}$. Results from the measurements on (*Z*)-5-ethylidene-2-norbornene gave an ideal-gas enthalpy of formation of $\Delta_f H^\circ_m[(Z)\text{-}C_9H_{12}, g, 298.15\ K] = (146.73 \pm 0.89)\ kJ\cdot mol^{-1}$, in excellent agreement with the value derived using group-additivity parameters. Hence the value for the strain energy in the bicyclo[2.2.1]hept-2-ene ring system of 84.9 kJ·mol^{-1} derived in earlier DIPPR 871 research was confirmed. The literature value (Kozina et al., 1972) for the ideal-gas enthalpy of formation of (*E*)-5-ethylidene-2-norbornene, $\Delta_f H^\circ_m(E)\text{-}C_9H_{12}, g, 298.15\ K] = (150.4 \pm 2.0)\ kJ\cdot mol^{-1}$, seems in error, and a value of $\Delta_f H^\circ_m[(E)\text{-}C_9H_{12}, g, 298.15\ K] = 141.8\ kJ\cdot mol^{-1}$ was derived using the group-additivity parameters.

The measured ideal-gas enthalpy of formation of 1,2-epoxy-3-phenoxypropane, $\Delta_f H^\circ_m(C_9H_{10}O_2, g, 298.15\ K) = -(99.68 \pm 1.06)\ kJ\cdot mol^{-1}$, differs from the summation of the group-additivity parameters by 8 kJ·mol^{-1}. Further work on aliphatic and aromatic ethers is required to reconcile the various sets of group parameters. The group-additivity parameters for alkenes listed in Table 14 of Steele and Chirico (1990) are now well established.

A value of −4.5 kJ·mol^{-1} was derived for the $C-(N)(C)_2(CO)$ group-additivity parameter. A value of 63 kJ·mol^{-1} was derived for the $C-(S)_2(C)_2$ group-additivity parameter. The sum of the $(CO)-(C_d)(C)$ and $C_d-(CO)(C_d)(H)$ group parameters is −95.0 kJ·mol^{-1}. [A value of−115.9 kJ·mol^{-1} was derived for the $(CO)-(C_d)(C)$ group-additivity parameter provided that 20.9 kJ·mol^{-1} is used for the $C_d-(CO)(C_d)(H)$ group.] Additional enthalpy of formation measurements on compounds that contain one but not both groups would be beneficial in resolving the discrepancies that still exist in the literature.

In addition values of the critical properties [$T_c = (605 \pm 1)$ K with $\rho_c = (278 \pm 10)\ kg\cdot m^{-3}$, $p_c = (4000 \pm 100)$ kPa] were derived for mesityl oxide and correspondingly [$T_c = (495 \pm 1)$ K, $\rho_c = (238 \pm 10)\ kg\cdot m^{-3}$, $p_c = (3290 \pm 100)$ kPa] for 4-methylpent-1-ene.

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