thermochimica acta

Thermochimica Acta 313 (1998) 101–110

Sublimation enthalpies at 298.15 K using correlation gas chromatography and differential scanning calorimetry measurements

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Received 20 June 1997; received in revised form 10 November 1997; accepted 11 November 1997

Abstract

The sublimation enthalpies of 17 hydrocarbons are obtained by combining the technique of correlation gas chromatography (CGC), to evaluate vaporization enthalpies at 298.15 K, and differential scanning calorimetry (DSC) to measure fusion enthalpies. Vaporization enthalpies at 298.15 K obtained by CGC are compared to values measured directly from vapor pressure measurements at temperatures above the melting point by adjusting the experimental vaporization enthalpy for the effects of temperature. Vaporization enthalpies obtained by these two methods agree within ±3877 J mol^{-1}. Fusion enthalpies are similarly adjusted for temperature. Sublimation enthalpies, obtained by combining temperature adjusted fusion, and vaporization enthalpies agree within ±2580 J mol^{-1}. The sublimation enthalpies of azulene and 1,8-cyclotetradecadiyne are also measured by head-space analysis resulting in values of 76880 and 94348 J mol^{-1} at 298.15 K, respectively. © 1998 Elsevier Science B.V.

Keywords: Correlation gas chromatography; Sublimation enthalpy; Vaporization enthalpy

1. Introduction

Sublimation enthalpies are an important macroscopic measure of the magnitude of intermolecular interactions in the solid state [1]. A variety of experimental techniques have been developed to measure sublimation enthalpies. These include measurements of mass transport by means of gas saturation techniques, Knudsen and torsion effusion, head-space analysis and calorimetry [2]. Many of these techniques require both, sophisticated equipment and highly trained personnel or involve measurements that are time-consuming and labor-intensive. Recently, we documented how a simple gas chromatographic technique could be used to obtain enthalpies of vaporization at 298.15 K [3]. We have now applied this technique to a series of 17 solid hydrocarbons, and have obtained vaporization enthalpies for these solids at 298.15 K. Combining these vaporization enthalpies with experimental fusion enthalpies adjusted to 298.15 K, using a protocol recently described, results in reliable sublimation enthalpies [4]. This report illustrates how this protocol can be applied to obtain accurate sublimation enthalpies. Included in the 17 hydrocarbons are two compounds with reported sublimation enthalpies of questionable value. The sublimation enthalpy of these two compounds are measured both by DSC-CGC and head-space analysis.

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PII S0040-6031(97)00432-2

2. Theoretical

2.1. Sublimation enthalpies

Accurate measurements of sublimation enthalpy can be obtained by combining the results of Eq. (1) with those of Eqs. (2) and (3) [4]. Eq. (1) is a thermodynamic equality which provides accurate sublimation enthalpies at the melting point of a solid, T_{fus}. Vaporization enthalpies can be adjusted from 298.15 K to T_{fus} by using Eq. (2). The sublimation enthalpy obtained at T_{fus}, can then be adjusted back to 298.15 K by using Eq. (3) as has been documented recently [4,5]:

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(T_{\mathrm{fus}}) = \Delta_{\mathrm{vap}}H_{\mathrm{m}}(T_{\mathrm{fus}}) + \Delta_{\mathrm{fus}}H_{\mathrm{m}}(T_{\mathrm{fus}}) \tag{1}$$

$$\begin{aligned}\Delta_{\mathrm{vap}}H_{\mathrm{m}}(T_{\mathrm{fus}}) &= \Delta_{\mathrm{vap}}H_{\mathrm{m}}(298.15\,\mathrm{K}) \\ &\quad + [10.58 + 0.26C_{\mathrm{Pl\,estd}}(298.15\,\mathrm{K})] \\ &\quad \times (298.15 - T_{\mathrm{fus}})\end{aligned} \tag{2}$$

$$\begin{aligned}\Delta_{\mathrm{sub}}H_{\mathrm{m}}(298.15\,\mathrm{K}) &= \Delta_{\mathrm{sub}}H_{\mathrm{m}}(T_{\mathrm{fus}}) \\ &\quad + [0.75 + 0.15C_{\mathrm{Pc\,estd}}(298.15)] \\ &\quad \times (T_{\mathrm{fus}} - 298.15)\end{aligned} \tag{3}$$

The symbols $C_{\mathrm{Pl\ estd}}$ and $C_{\mathrm{Pc\ estd}}$ in Eqs. (2) and (3) refer to the heat capacities of the liquid and solid phases of the compound in question at 298.15 K and can be estimated by group additivity [6]. The reliability of Eqs. (1)–(3) has been tested against experimental data. Sublimation enthalpies obtained by using Eqs. (1)–(3) have been compared to results measured directed for a series of 117 compounds. A standard deviation of $\pm 4210\ \mathrm{J\,mol^{-1}}$ was observed between experimental sublimation enthalpies measured directly and those obtained through the use of Eqs. (1)–(3) [4].

2.2. Correlation gas chromatography and head space analysis

Gas chromatography has previously been used to measure thermodynamic properties of solutions. Recently, we reported a simple modification of a technique used by Peacock and Fuchs [7] to obtain vaporization enthalpies of a variety of simple organic molecules including hydrocarbons. The procedure has been detailed previously [3]. A brief outline is provided below, using the data in Table 1 as an example.

Included among the compounds measured previously [3] were a few hydrocarbons that are solids at 298.15 K. If the retention time measured by the gas chromatograph is inversely proportional to the vapor pressure of the solute in solution on the stationary phase of the column, then the enthalpy of transfer ($\Delta^{v}_{\mathrm{sln}}H_{\mathrm{m}}(\overline{T})$) that is measured from a study of the temperature dependence of retention time should be independent of the physical state of the material at 298.15 K. Correlation of $\Delta^{v}_{\mathrm{sln}}H_{\mathrm{m}}(\overline{T})$ with the $\Delta_{\mathrm{vap}}H^{0}_{\mathrm{m}}$ (298.15 K) of the compounds with known vaporization enthalpies should provide reasonable values of $\Delta_{\mathrm{vap}}H^{0}_{\mathrm{m}}$ (298.15 K) for the solids whose vaporization enthalpies at 298.15 K are presumably unknown, provided both, retention times and vaporization enthalpies are properly bracketed by the standards [3].

Vaporization enthalpies at 298.15 K, obtained for the liquid state of solids, when added to their respective fusion enthalpies corrected to 298.15 K result in reasonable estimates of their sublimation enthalpies [3,4,8]. We would now like to report the application of this technique using the protocol described above (Eqs. (1)–(3)) to evaluate the sublimation enthalpy of a total of 17 solid hydrocarbons. It should be emphasized that the vaporization enthalpies of these

Table 1
Retention time (min) at T°C

Compound	220	230	240	250	260	270
CCl_4	2.70	2.726	2.747	2.77	2.804	2.833
Hexadecane	3.853	3.622	3.467	3.354	3.266	3.211
trans-Stilbene	4.785	4.354	4.044	3.817	3.642	3.52
Anthracene	5.70	5.069	4.607	4.269	4.006	3.818
Eicosane	7.331	6.110	5.259	4.679	4.256	3.965
Docosane	11.822	9.179	7.38	6.186	5.340	4.761

solids obtained by correlation gas chromatography can be hypothetical yet thermodynamically relevant numbers, as shown below. This is demonstrated in a number of cases where the vaporization enthalpy of the liquid state of the solid is available in the literature at temperatures above the melting point. Adjustment of the vaporization enthalpy from some mean temperature of measurement, $\overline{T}$, to 298.15 K using Eq. (2) gives good agreement with the value measured by correlation gas chromatography. Combination of the vaporization enthalpy with the corresponding fusion enthalpy, according to the protocol defined by Eqs. (1)–(3), results in a sublimation enthalpy which compares very favorably to the value measured directly [4].

In addition to using literature values for comparison of sublimation enthalpies, obtained by the combined DSC-CGC method, we would also like to report the sublimation enthalpies of 1,8-cyclotetradecadiyne and azulene measured directly by head-space analysis. Measurement of the sublimation enthalpy of 1,8-cyclotetradecadiyne has been repeated because of a large discrepancy observed between the value, calculated using Eqs. (1)–(3) (94 348 J mol^{-1}, Table 6) and the literature value of (166 000 J mol^{-1}, [9]). The sublimation enthalpy of azulene has been reported several times. These enthalpies are summarized in Table 5. For a molecule with many physical properties markedly similar to naphthalene, a standard in sublimation calorimetry, agreement between three out of the four reported values is quite poor. This prompted us to measure this value again, both by head-space analysis and by the combined protocol of DSC-CGC and associated Eqs. (1)–(3). The results of using the combined protocol of DSC-CGC for both 1,8-cyclotetradecadiyne and azulene are reported in Table 6.

3. Experimental

3.1. Instrumentation and procedure-correlation gas chromatography

All the gas chromatographic experiments described here were performed on a Hewlett–Packard Model 5890 Series II Gas Chromatograph equipped with a split/splitless capillary injection port and a flame-ionization detector. The column temperature was monitored independently using a Kluke 51 K/J thermometer. Additional details of the equipment and of the procedure have been described previously [3]. Retention-time data for the 17 compounds listed in Table 6 along with the standards used have been reported [3,8,10]. Some data are included in Table 1 and the protocol used in treating the data is discussed below. Results for the seventeen compounds listed in Tables 5 and 6 are in most instances averages of a variety of experiments, some from duplicate runs, others from experiments performed under different conditions of temperature, column and internal standards (various *n*-alkanes). Typical columns used include the following: 30 m DB-5, 60 m DB-5MS, and a 30 m HP-1 column. The standard deviations associated with the reproducibility of the experiments reported in the second column of Table 5 varied from 300 to 700 J mol^{-1}. The literature values used for the *n*-alkanes C_{10}–C_{20} are those recently recommended by Ruzicka and Majer [11] and, for C_{21}–C_{28}, those recommended by Chickos and Wilson [12].

3.2. Instrumentation and procedure-head-space analysis

The procedure used in head-space analysis has been detailed previously [2]. 1,8-Cyclotetradecadiyne, purchased from K and K Laboratories was recrystallized from acetone, mp 96.7–97.3°C ([9]). The sample was assayed as 99.93% pure by gas chromatography on a 5 m×0.53 mm DB-1 Megabore capillary column. Two impurities with longer retention times were also observed. ^{1}H and ^{13}C NMR confirmed both the chemical composition and purity of the sample. An infrared spectrometer, a PE Model 783 equipped with a data station was used in these experiments. Absorbances were calibrated with prepared standard solutions of 1,8-cyclotetradecadiyne in a matched set of 0.2 mm NaCl solution cells by measuring the absorbance at 2927 cm^{-1} relative to the baseline at 3050 cm^{-1} in carbon tetrachloride. Sixteen values of vapor pressures, varying from 0.6 to 55 Pa, were measured over the 315–364 K range. It is important to recognize that while the temperature dependence of the vapor pressure measured by head-space analysis is reliable, the actual value of the vapor pressures is not, and vapor pressures as determined by head-space analysis should be considered only as approximate values. The results are shown in columns 1–4 of Table 3.

A sample of azulene, kindly provided to us by Professor William Herndon, was determined to be 99.46% pure as assayed by gas chromatography on a 30 m×0.32 mm DB-5 capillary column, mp 99.2–100°C (99–100.5°C [18]). It was observed that three impurities eluted later than azulene. Vapor pressures were determined by a quantitative infrared analysis of the condensed vapors trapped from the steady-state head-space experiments in carbon tetrachloride. A Perkin–Elmer Model 1600 FTIR was used in the analysis. Absorbances were calibrated with prepared standard solutions of azulene in a single 0.2 mm NaCl solution cell by measuring the net absorbance at 1392 cm^{-1} and the baseline at 1350 cm^{-1}. Measurements were made on 16 vapor-pressure values over the 283.3–325.6 K range, resulting in vapor pressures in the 0.3–25 Pa range. The results are shown in columns 5–8 of Table 3.

3.3. Differential scanning calorimetry

Fusion enthalpies were determined on a Perkin–Elmer Model DSC-2 differential scanning calorimeter interfaced to a computer and calibrated with indium metal (28700±330 J mol^{-1} [23]). All analyses were performed in triplicate. The fusion enthalpy of azulene measured in a standard aluminum sample pan was 19200±500 J mol^{-1}. Upon reweighing the sample, a 3–8% weight loss was detected. Repetition of this set of experiments using stainless-steel high-pressure capsules (PE B018-2901) resulted in a value of 17530±800 J mol^{-1} with no detectable weight loss. Similarly, for adamantane, a fusion enthalpy of 10910±800 J mol^{-1} was measured using the high pressure cells.

4. Results and discussion

4.1. Vaporization enthalpies of trans-stilbene and anthracene

In the correlation gas chromatography experiments, the dead volume of the column is generally obtained by measuring the retention time of an unretained component injected in the mixture. In the experiments described in Table 1, the solvent carbon tetrachloride is not retained on the column and its retention time is used for this measurement. As the temperature is increased, the viscosity of the helium carrier gas increases and the flow rate decreases, thereby increasing the retention time of carbon tetrachloride $(rt_{\mathrm{CCl_4}})$. Differences in the retention time of the hydrocarbons relative to that of carbon tetrachloride measure the amount of time spent by the solute on the column. This time is inversely proportional the vapor pressure of the solute in solution. A plot of $\ln(1/(rt_{\mathrm{solute}} - rt_{\mathrm{CCl_4}})$ against $1/T$ (K^{-1}) results in a straight line as characterized by the correlation coefficient, r^2, given in the third column of Table 2. Correlation coefficients of less than 0.99 are usually an indication of some retention of the component used to measure the dead volume. The slope of the line multiplied by the gas-constant results in the enthalpy of transfer from solution to the vapor, $\Delta_{\mathrm{sln}}^{v}H_{\mathrm{m}}$, column 2 of Table 2. A second correlation between $\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}$ (298.15 K) and, columns 2 and 4 of Table 2, results in Eq. (4). This relationship is used to evaluate the vaporization enthalpies of the unknowns. The vaporization enthalpies reported for *trans*-stilbene and anthracene in Table 2 are derived from Eq. (4); those reported in Tables 4 and 6 are averages of several determinations by gas chromatography.

Table 2
Enthalpies (in J mol^{-1})

Compound	$\Delta_{\mathrm{s\,ln}}^{\mathrm{v}}H_{\mathrm{m}}$	Correlation coefficient r^2	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}$ (298.15 K) (lit)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}$ (298.15 K) (calc)
Hexadecane	49 467	0.9996	81 400	80 860
Eicosane	62 759	0.9999	101 800	103 444
Docosane	69 265	0.9999	115 600	114 496
trans-Stilbene	49 381	0.9999		80 713
Anthracene	49 571	0.9998		81 036

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}(298.15\,\mathrm{K}) = 1.699(\pm 0.144) \times \Delta_{\mathrm{sln}}^{v}H_{\mathrm{m}}(518.2\,\mathrm{K}) - 3188(\pm 2050); \quad r^2 = 0.9929 \tag{4}$$

4.2. Sublimation enthalpies of 1,8-cyclotetradecadiyne and azulene

The sublimation enthalpies of 1,8-cyclotetradecadiyne and azulene were obtained from a Clausius–Clapeyron treatment of the data in Tables 1 and 3. A plot of ln(vapor pressure) against $1/T\,(\mathrm{K}^{-1})$ resulted in Eqs. (5) and (6) for 1,8-cyclotetradecadiyne and azulene, respectively.

$$\ln P = -10\,535(1/T) + 33.0; \quad r^2 = 0.9972; \quad \Delta_{\mathrm{sub}}H_{\mathrm{m}}(338) = 87\,580 \pm 1000\,\mathrm{J\,mol^{-1}} \tag{5}$$

$$\ln P = -9434(1/T) + 32.22; \quad r^2 = 0.9979; \quad \Delta_{\mathrm{sub}}H_{\mathrm{m}}(303) = 78\,430 \pm 1300\,\mathrm{J\,mol^{-1}} \tag{6}$$

This resulted in sublimation enthalpies of 89 410 and 78 550 J mol^{-1} for 1,8-cyclotetradecadiyne and azulene when the results were adjusted to 298.15 K using Eq. (3). Sublimation enthalpies obtained by head-space analysis are accurate to within ±5% and, generally, result in values a few % lower than those obtained by other techniques [2].

The sublimation enthalpy of 89 410 J mol^{-1} (298.15 K) for 1,8-cyclotetradecadiyne measured in this work is considerably smaller than the value of 166 000 J mol^{-1} reported previously [9]. A similar discrepancy has been noted for the value reported for cyclotetradecane [9,14,31]. The result of 78 550 J mol^{-1} (298.15 K) for azulene is in good agreement with two of the four values reported previously and suggest that the sublimation enthalpy is slightly larger than the value accepted for naphthalene. This is consistent with the more polar nature associated with the structure of azulene. These results along with other literature values are summarized in Table 5 and compared to the DSC-CGC results in Table 6.

4.3. Vaporization enthalpies of solids by correlation gas chromatography

Many of the solids selected to test the DSC-CGC results were chosen because vaporization and/or sublimation enthalpies are readily available. All vaporization enthalpies were calculated from vapor-pressure measurements performed at temperatures

Table 3
Vapor pressure of 1,8-cyclotetradecadiyne and azulene as a function of temperature as determined by head-space analysis

1,8-Cyclotetradecadiyne				Azulene			
Sample temp./ K	Bulb temp./ K	Sample size/ mg	Vapor pressure/ Pa	Sample temp./ K	Bulb temp./ K	Sample size/ mg	Vapor pressure/ Pa
315.2	397	0.438	0.62	283.3	379	0.163	0.342
323.2	397	0.939	1.33	283.4	379	0.149	0.314
323.2	398	1.018	1.446	283.9	379	0.184	0.388
323.2	398	0.977	1.387	293.4	381	0.511	1.081
330	399	2.283	3.392	293.5	381	0.430	0.909
330	399	2.331	3.318	293.6	379	0.597	1.256
330	399	2.286	3.255	293.6	379	0.512	1.077
343	400	6.088	8.677	303.3	369	1.470	3.013
343	400	6.876	9.801	303.4	372	1.595	3.297
353.1	401	16.37	23.43	303.4	377	1.520	3.185
353.1	402	16.69	23.93	315.8	379	5.365	11.3
353.2	403	17.53	25.21	315.8	379	4.903	10.33
363.8	403	38.03	54.69	316	379	5.121	10.78
363.8	404	38.57	55.5	324.8	381	11.00	23.25
363.8	404	38.53	55.51	325.1	381	11.17	23.64
				325.6	381	11.89	25.17

Table 4
Vaporization enthalpies of a series of solid hydrocarbons

Compound	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}$ (298.15 K) by GC/ (J mol^{-1})	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}(\overline{T})$/ (J mol^{-1}) ($\overline{T}$/K) lit. [a]	$C_{\mathrm{Pl\ estd}}$/ (J mol^{-1} K^{-1})	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{0}$ (298.15 K)/ (J mol^{-1}) lit.
$C_{10}H_8$ azulene	58 192	52 999 (384)	205	58 483
$C_{10}H_8$ naphthalene	53 438	50 647 (367)	205	55 045
$C_{12}H_{10}$ biphenyl	66 244	57 275 (405)	249	65 312
$C_{12}H_{10}$ acenaphthene	66 210	60 342 (383)	244	66 618
$C_{12}H_{24}$ cyclododecane	63 017	52 576 (401)	311	61 975
$C_{13}H_{10}$ fluorene	72 340	54 229 (417)	282	63 567
$C_{14}H_{10}$ anthracene	79 812	58 568 (519)	279	76 936
$C_{14}H_{10}$ phenanthrene	78 650	69 617 (388)	279	77 090
$C_{14}H_{12}$ *trans*-stilbene	79 725	65 458 (434)	304	77 640
$C_{19}H_{16}$ triphenylmethane	94 552	58 601 (527)	395	84 551
$C_{24}H_{18}$ 1,3,5-triphenylbenzene	139 950	118 000 (477) [b]	484	142 408

[a] Ref. [20], unless noted otherwise.
[b] Ref. [22].

above the melting point of the solid. Most vaporization enthalpies were calculated from the Antoine Constants by a Clausius–Clapeyron treatment of vapor pressure with temperature. A temperature range of 30 K was used. Vaporization enthalpies were adjusted to 298.15 K, using Eq. (2), by replacing T_{fus} and terms associated with T_{fus} with values appropriate to the mean temperature, $\overline{T}$. Table 4 summarizes the vaporization enthalpy results. The vaporization enthalpies in column 2 are the values obtained by correlation gas chromatography. Literature values at temperature $\overline{T}$ (in parenthesis), are included in column 3 and were adjusted to 298.15 K using the estimated heat capacity of the liquid given in column 4. The adjusted values are listed in column 5. Comparison of the values in columns 2 and 5 results in a standard deviation of ± 3877 J mol^{-1} between the two sets of numbers. The agreement between the results obtained by CGC and the literature is very good, considering the necessary temperature extrapolations.

4.4. Sublimation enthalpies using DSC-correlation gas chromatography

Compounds chosen to test the accuracy of $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) measured by DSC-CGC were selected because of the availability and reliability of their sublimation enthalpies. These values are summarized in Table 5. This table includes sublimation enthalpy values available in the literature and identifies how experimental values were selected for the comparisons that follow. All sublimation enthalpies reported at temperatures other than 298.15 K have been adjusted to 298.15 K using Eq. (3) by replacing T_{fus} and terms associated with T_{fus} with values appropriate to the mean temperature of measurement, $\overline{T}$. The heat capacities used for each temperature adjustment were estimated. The $C_{\mathrm{Pc\ estd}}$ (298.15) values used for each of the compounds in Table 5 are included in Table 6.

Sublimation enthalpies obtained by the combined technique of CGC-DSC and associated equations can be compared to direct experimental measurements in Table 6. The second column of the table lists the vaporization enthalpies measured by correlation gas chromatography. The experimental fusion enthalpy for each compound is listed in column 3 followed by its melting point. The estimated heat capacities used in Eqs. (2) and (3) follow in the next two columns [6].

The sublimation enthalpy calculated according to Eqs. (1)–(3) is listed in column 7 and the experimental sublimation enthalpy obtained from Table 5 is listed in the last column. A comparison of these two columns results in a standard deviation of ± 2580 J mol^{-1}. This uncertainty is similar to the uncertainty generated by a direct comparison of the experimental literature values in Table 5 and suggests that the protocol described by combining CGC with DSC, and adjusting the resulting enthalpies for temperature is equally useful for obtaining reliable sublimation enthalpies.

Table 5
Recommended sublimation enthalpies of selected hydrocarbons at 298.15 K

Compound			Compound		
Literature value [Ref.] [a]	Value selected	Comments	Literature value [Ref.] [a]	Value selected	Comments
tri-t-butylmethane			*acenaphthylene*		
58 600 [8]	57 820±1110	Average of first two entries	73 330 [18]	72 510±1150	Average of all entries; recommended value
57 030 [16]			73 000 [19]		
7700 [17]			71 200 [20]		
azulene			*trans-stilbene*		
82 900 [20]	76 880±1630	Average of second, third and fourth entries	104 400 [26]	102 400±1870	Average of top three entries; recommended value
78 550 [b]			100 700 [27]		
75 300 [21]			102 100 [28]		
76 800 [19]			61 100 [29]		
95 400 [25]			99 200 [19]		
naphthalene			*1,8-cyclotetradecadiyne*		
72 600 [30]	72 600±300	IUPAC recommendation	166 000 [9]	89 410±1000	This work
			89 410 [b]		
cyclotetradecane			*acenaphthene*		
98 520 [14]	92 170±5500	Average of first, third and fourth entries	86 940 [18]	85 310±1580	Average of all entries; recommended value
134 950 [9]			83 400 [33]		
89 300 [31]			86 200 [34]		
88 700 [32]			84 700 [35]		
diphenylacetylene			*triphenylmethane*		
95 100 [36]	95 100±1100	First Entry	116 390 [39]	112 320±5800	Average of top two entries
90 000 [37]			108 250 [40]		
88 700 [38]			101 860 [41]		
fluorene [c]			*adamantane*		
81 500 [42]	86 130±2170	Average of last three entries	58 450 [47]	58 810±2090	Average of all entries recommended value
80 200 [43]			60 540 [48]		
92 880 [44]			60 140 [49]		
88 600 [18]			54 800 [50]		
85 300 [46]			59 300 [51]		
84 500 [46]			59 600 [52]		
anthracene			*phenanthrene*		
100 240 [53]	99 220±2910	Average of all entries	90 900 [57]	91 810±2140	Average of all entries
103 880 [44]			95 160 [18]		
96 800 [54]			92 500 [58]		
97 400 [55]			89 570 [33]		
97 800 [56]			90 900 [19]		
cyclododecane			*biphenyl*		
76 400 [59]	76 400±1400	Only value	83 780 [39]	82 030±1210	Average of all entries
			81 500 [13]		
			81 020 [48]		
			81 800 [19]		
1,3,5-triphenylbenzene					
152 000 [22]	149 545±1893	Average of all entries			
149 700 [45]					
147 430 [24]					
149 070 [20]					

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[a] All enthalpies: J mol^{-1} at 298.15 K.
[b] Head-space analysis, this work.
[c] Only the most recent five or six references were used.

Table 6
Comparison of experimental sublimation enthalpies with values determined by combined DSC-CGC

Compound	$\Delta_{vap}H_m$ (298.15 K)/ (J mol^{-1})	$\Delta_{fus}H_m$ [a]/ (J mol^{-1})	T_{fus}/ K	$C_{Pc\ estd}$ [f]/ (J mol^{-1} K^{-1})	$C_{Pl\ estd}$ [f]/ (J mol^{-1} K^{-1})	$\Delta_{sub}H_m$ (298.15 K)/ (from Eqs. (1)–(3))	(from Table 4)
$C_{10}H_8$ azulene	58 192	17 530 [b]	374	157	205	72 731	76 880
$C_{10}H_8$ naphthalene	53 438	19 100	353	157	205	70 367	72 600
$C_{10}H_{16}$ adamantane	52 007	10 910 [b]	541	194	238	52 569	58 810
$C_{12}H_8$ acenaphthylene	64 344	6940	327	171	236	69 970	72 510
$C_{12}H_{10}$ acenaphthene	66 210	21 460	366	188	244	84 612	85 350
$C_{12}H_{10}$ biphenyl	66 244	18 660	342	192	249	82 897	82 030
$C_{12}H_{24}$ cyclododecane	6 3017	14 800 [c]	334	295	311	76 152	76 400
$C_{13}H_{10}$ fluorene	72 340	19 580	388	199	262	87 599	86 130
$C_{13}H_{28}$ tri-t-butylmethane	55 859	3100 [d]	357	323	379	55 433	57 820
$C_{14}H_{10}$ diphenylacetylene	7 6815	20 502	334	223	306	95 312	95 100
$C_{14}H_{10}$ phenanthrene	7 8650	15 720	374	209	279	90 500	91 810
$C_{14}H_{10}$ anthracene	79 812	29 372	489	209	279	99 447	99 220
$C_{14}H_{12}$ *trans*-stilbene	79 725	27 600	398	235	304	101 971	102 400
$C_{14}H_{20}$1,8-cyclotetradecadiyne	7 5784	22 600	370	303	353	94 349	89 410
$C_{14}H_{28}$ cyclotetradecane	6 8459	28 700	328	344	363	95 589	92 170
$C_{19}H_{16}$ triphenylmethane	9 4552	21 979	365	297	395	111 987	112 320
$C_{24}H_{18}$ 1,3,5-triphenylbenzene	13 9950	22 928 [e]	446	366	484	150 936	149 545

[a] Fusion enthalpies are from Ref. [15], unless noted otherwise.
[b] This work.
[c] From Ref. [60].
[d] From Ref. [17].
[e] From Ref. [22].
[f] From Ref. [6].

The sublimation enthalpy of adamantane requires some additional comment. It has previously been shown that extrapolations using Eqs. (2) and (3) are valid from 200 to 500 K [4]. Since melting point of adamantane is 541 K, temperature adjustments using these two equations for this compound are likely to be less reliable.

5. Summary

The sublimation enthalpies obtained by head-space analysis and combined DSC-CGC for both, 1,8-cyclotetradecadiyne and azulene are in good agreement with each other. The agreement obtained confirms that the literature value for reported for 1,8-cyclotetradecadiyne is in error. The value measured for azulene by head-space analysis, 78 850 J mol^{-1}, compares quite favorably with two of the literature values. A mean value of 76 880 J mol^{-1} was selected on this basis. The value measured by the combined CGC-DSC of 72 731 J mol^{-1} is somewhat less than this but the results obtained for both 1,8-cyclotetradecadiyne and azulene are within the ±4200 J mol^{-1} accuracy that characterizes this protocol [4].

The results of these experiments demonstrate the applicability of the combined DSC-CGC technique on hydrocarbons. In principle, this method should work equally as well for any class of compounds shown to give reliable vaporization enthalpies by CGC [3]. Advantages of the method include small sample requirements and ease of measurement. The protocol described above accommodates measurements performed at different temperatures, including the use of hypothetical as well as actual phase change enthalpies.

Acknowledgements

Financial support from the Research Board of the University of Missouri is gratefully acknowledged.

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