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Enthalpies of Formation of Small Linear Carbon Clusters

Karl A. Gingerich,* Heidi C. Finkbeiner, and Richard W. Schmude, Jr.

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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Abstract: The high-temperature Knudsen effusion mass spectrometric method was used in measuring the equilibrium partial pressures of C_1–C_7 above pure graphite. These data were combined with new thermal functions for linear C_4–C_7, which were calculated from recent spectroscopic and theoretical data in evaluating enthalpies of formation for C_2–C_5. The following enthalpies of formation, $\Delta_fH(C_n,g,0)$ and of atomization, $\Delta_aH(C_n,g,0)$, in kJ mol^{-1}, were obtained on the basis of the third law method: C_2, 817 ± 8 and 605 ± 8; C_3, 831 ± 13 and 1303 ± 13; C_4, 1052 ± 16 and 1793 ± 17; and C_5, 1081 ± 16 and 2475 ± 17. The enthalpies of formation for C_4 and C_5 are higher than previously believed. They are in good agreement with recent theoretical predictions.

I. Introduction

Small carbon clusters have been the object of many investigations in recent years because they are of considerable interest in several scientific fields. Carbon clusters have been considered as precursors of soot.[1,2] They have been observed in flames[1] and in stellar[3,4] and cometary spectra[5] among other subjects. An extensive review on carbon molecules, ions, and clusters was recently given by Weltner and Van Zee.[6] The rapid development of experimental techniques and theoretical computations has led to an increasing interest in small carbon clusters and with it more accurate molecular properties, such as geometry, bond distances, vibrational and electronic structure, and ionization potentials. The recent synthesis of solid C_{60}[7] has given a tremendous boost to the interest in carbon clusters of a large range of sizes.

Relative to the amount of research done on carbon clusters, little progress has been made on the determination of their thermodynamic properties, such as enthalpies of formation and atomization energies. Diatomic and triatomic carbon have been the object of a number of investigations, yet there are still some uncertainties in the thermodynamic properties of C_3.[6] The only report on experimental thermodynamic properties of C_4 and C_5 has been by Drowart et al.[8] Since these results have been reported and reviewed,[9,10] considerable new experimental and theoretical information on the molecular structure of small carbon clusters to about C_{10} has become available. This new information now permits the calculation of reliable thermal functions for these molecules and consequently the determination of more accurate third law enthalpies of formation from measured equilibrium pressures.

The capabilities of theoretical computations have in recent years sufficiently advanced to predict binding energies (heats of dissociation or atomization). Thus Raghavachari and Binkley[11] have calculated the binding energies of C_2–C_{10} and predicted the enthalpies of formation for C_6–C_{10} on the basis of these calculations, scaled to agree with the thermodynamic results for C_2–C_5.[8] Martin et al. have improved these predictions by calculating up-to-date thermal functions for C_4[12] and C_5[13] and basing the new scaling factors on the corresponding revised enthalpies of formation for C_4 and C_5 from mass spectrometric equilibrium measurements.[8]

In the present investigation, we present the results of a Knudsen effusion mass spectrometric investigation of the equilibrium partial pressures of C_2–C_7 above graphite. For C_4–C_7, the partial pressures have been combined with new thermal functions calculated from theoretical and experimental molecular constants, and reliable enthalpies of formation and binding energies (enthalpies of atomization) have been obtained. The results for C_2–C_5 are compared with literature data and for C_4 and C_5 with revised values[12,13] from the study by Drowart et al.[8] The results from this investigation for C_6[14] and C_7[15] have previously been reported.

II. Calculation of Thermal Functions

Many experimental and theoretical studies have been performed on the measurement and theoretical prediction of molecular parameters for small carbon clusters. This new knowledge has been used in the calculation of the Gibbs enthalpy, $-[G(T) - H(0)]/T$, and heat content functions, $H(T) - H(0)$, of these molecules, employing standard statistical thermodynamic relations[16] in the harmonic oscillator, rigid-rotor approximation. The results of these calculations for C_6(g) and C_7(g) have previously been presented.[14,15]

A. C_4. The linear and rhombus structures of C_4 are predicted to be nearly isoenergetic.[12] Both structures have been detected experimentally.[17,18] Slanina[19] has shown that at the temperatures

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of our measurements the rhombus isomer contributes less than 10% to the equilibrium vapor; therefore we have considered only the linear structure in our evaluations.

The bond lengths for the linear structure, 1.313 and 1.288 Å (center), were calculated from the rotational constant reported by Heath and Saykally[20] and the MBPT(4) bond lengths reported by Magers et al.[21] A moment of inertia of 104.6 amu Å^2 is calculated from the bond lengths by Magers et al., whereas that obtained from the experimental value for the rotational constant is 101.9 amu Å^2.[20] The two values were brought into agreement by multiplying the MBPT(4) bond lengths by a scaling factor of 0.9869. Heath and Saykally[20] report an experimental antisymmetric stretching frequency for C_4 of ν_3 = 1548.9 cm^{-1} based on gas-phase spectroscopy, while Shen and Graham[22] report a frequency of ν_3 = 1543.4 cm^{-1} based on matrix isolation spectroscopy. Shen and Graham measured the ν_3 antisymmetric stretching frequency for eight different isotopomers of C_4. With these frequencies, they carried out a Wilson GF evaluation and determined the C–C force constants and interaction terms. From these they predicted the two symmetric stretching vibrations as 2164 and 919 cm^{-1}, which we used in our evaluation of the thermal functions together with the antisymmetric vibrational frequency (in cm^{-1}) of ν_3 = 1549.[20]

The three stretching frequencies, 1549, 2164, and 919 cm^{-1}, were compared to the MBPT(2) frequencies reported by Michalska et al.,[23] and a scaling factor of 0.982 was calculated and applied to the two doubly degenerate bending frequencies, yielding 411 and 184 cm^{-1}, respectively, which we used in the thermal functions evaluation. Graham et al.[24] report transition energies of 19 564 ($^3\Sigma_u^-$ state) and <6000 cm^{-1} ($^3\pi_g$ state). The remaining transition energies (and their degeneracies) of 2041 (2), 2065, 9267 (6), and 21 059 (3) cm^{-1} used in the thermal functions evaluation were taken from the SDTQ predictions of Magers et al.[21]

B. C_5. Several groups have reported a ground-state rotational constant for C_5,[4,25–27] and the values agree within the reported uncertainties. We have selected the rotational constant reported by Bernath et al.[4] because of the reported lower uncertainty. The bond lengths of C_5, 1.286 and 1.280 Å (between center atoms), were calculated by multiplying the CEPA-1 bond lengths of Botschwina and Sebald[28] by a scaling factor of 0.9978. This resulted in a moment of inertia in agreement with the selected experimental value.

The three bending frequencies (in cm^{-1}) used, $\nu_5(\pi_g)$ = 219, $\nu_6(\pi_u)$ = 524, and $\nu_7(\pi_u)$ = 108, are the averages of the values reported by Moazzen-Ahmadi et al.,[26] Arnold et al.,[18] and Kitsopoulos et al.[29] The antisymmetric vibrations (in cm^{-1}), ν_3 = 2169[25–27] and ν_4 = 1447,[30] have been measured experimentally. Arnold et al.[18] report that ν_2 = 798 ± 45 cm^{-1}, based on photoelectron spectra, which they point out is in agreement with theoretical predictions and the value calculated from matrix isolation spectra by Vala et al.[31] from the Wilson GF method.

Table 1. Gibbs Energy Functions, $[G(T) - H(0)]/T$ (in J mol^{-1} K^{-1}), and Heat Content Functions, $H(T) - H(0)$ (in kJ mol^{-1}), for C_4 and C_5

	C_4		C_5	
T (K)	$-[G(T) - H(0)]/T$	$H(T) - H(0)$	$-[G(T) - H(0)]/T$	$H(T) - H(0)$
298.15	210.31	13.47	221.74	16.565
2500	342.20	197.65	383.85	239.33
2600	345.32	206.92	387.61	250.34
2700	348.33	216.21	391.26	261.37
2800	351.25	225.51	394.79	272.43
2900	354.08	234.84	398.21	283.52
3000	356.84	244.18	401.53	294.65

The final vibration, $\nu_1(\sigma_g)$, is selected as 1904 cm^{-1}, based on the Wilson GF evaluation by Vala et al.[31] It is felt that this value is reliable since it is based on force constants that were calculated from 20 different isotopomers of the $\nu_3(\sigma_u)$ vibration. Energies and multiplicities of excited electronic levels come from the CI study of Pacchioni and Koutecky.[32] The multiplicity (1.0) of the ground state is based on several theoretical predictions. Our computed thermal functions for C_4 and C_5 are listed in Table 1.

III. Experimental Section

A single-focusing 90° sector magnetic deflection mass spectrometer was employed. The mass spectrometer, the Knudsen effusion cell assembly details, and the experimental procedures used in this investigation have been described previously.[33,34] The Knudsen cell was made from tantalum into which an inner, close-fitting cell of ultracarbon UFS graphite was inserted. Both cells had coaxial, tapered orifices of 0.51-mm diameter and 0.25-mm combined length (half of the dimensions given in ref 15). The graphite cell was charged with a mixture of cerium, rhodium, ruthenium, and osmium to which graphite powder in substantial excess was added, to ascertain unit activity of graphite during the entire investigation. A weighted small amount of silver was added for calibration purposes. The presence of the liquid metal alloy at the temperatures of investigation of the carbon molecules served as a catalyst to assure unity vaporization coefficients for the measured carbon species.[35]

The energy of the ionizing electrons was 20 V, and the emission current was regulated at 1.0 mA. Temperatures were measured by sighting a Leeds and Northrup optical pyrometer at a threaded blackbody hole in the bottom of the tantalum cell. The pyrometer had previously been calibrated in situ at the melting point of gold. The ionic species were identified by their mass-to-charge ratio, m/e, isotopic abundance, and ionization efficiency.

The appearance potentials were determined by the linear extrapolation method, and the electron energy scale was calibrated using the ionization potentials of atomic silver (7.576 eV) and carbon (11.260 eV) as reference.[36] The values (in eV) are C_2, 11.6 ± 0.4; C_3, 12.1 ± 0.4; C_4, 11.6 ± 0.5; C_5, 11.5 ± 0.5; C_6, 10.2 ± 1.1; and C_7, 10.5 ± 1.2.

Besides the carbon species C_1–C_7 for which we report results, gaseous Ce, Rh, CeC_2, CeC_4, RhC, CeRh, Ru, and RuC were observed as important vapor components, together with minor amounts of other carbides. In the early stages of measurements, after silver had been evaporated, Ba^+ was observed. The measurements reported for C_1^+, C_2^+, and C_3^+ were begun after the sample had been heated for more than 40 h at temperatures between 2000 and 2300 K. The first observed species at mass 48, corresponding to the main peak of C_4, had an appearance potential of about 9 eV, indicating the presence of a metal, presumably Ti^+, as its parent. A similar observation had been made by Chupka and Inghram.[37] In our thermodynamic evaluation of C_4^+, we therefore included only measurements made above 2550 K and after heating for an additional 50 h between 2300 and 2600 K. We also, as a precaution, did not include the early measurements of m/e = 60 in our evaluation of C_5. A small peak, originating from the Knudsen cell, tentatively assigned to Al_2O, was observed near the position of C_6 (m/e

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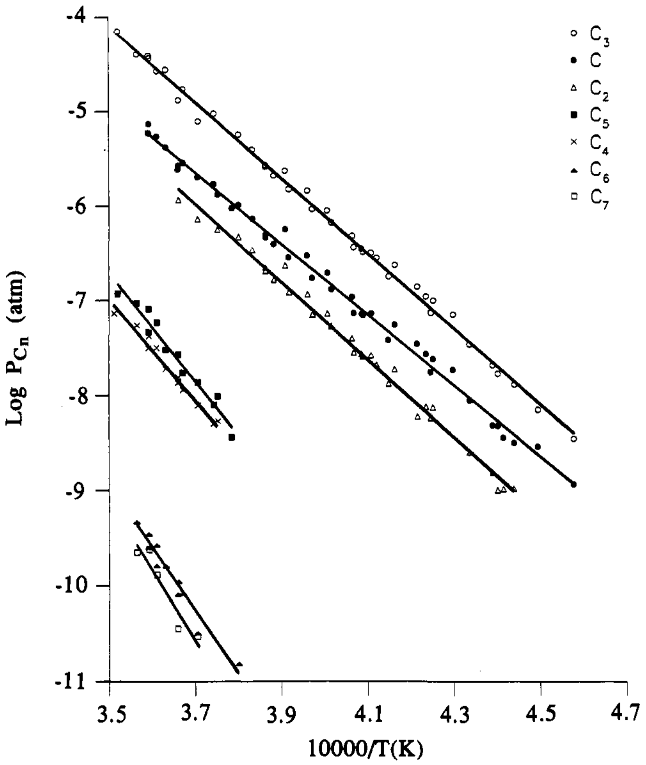

Figure 1. Plot of log P_{C_n} (n = 1–7) versus 10 000/T.

= 72) during the initial measurements. It was monitored and disappeared completely toward the end of the investigation.

A reference calibration constant, $k(C) = P(C)/I(C)T$, was obtained using the partial pressures for atomic carbon[38] and the measured ion currents of C^+, corrected for an estimated 10% fragment contribution from other carbon-containing species. This is considered a maximum correction for fragmentation from an analysis of several ionization efficiency curves taken for C^+. The resulting value for $k(C)$ was 0.161 atm A^{-1} K^{-1}. After cerium and rhodium had essentially been evaporated, a shift in the ion currents of C^+ was noted, yielding a reference calibration constant of 0.111 atm A^{-1} K^{-1} (identified as Series II in ref 14). This apparent increase in sensitivity is thought to be caused by a widening of the orifice of the Knudsen cell during the experiments. The measured ion currents of Series II, in the present manuscript, have been adjusted to correspond to $k(C) = 0.161$. From this value the corresponding constants, $k(C_n)$, have been derived using

$$k(C_n) = \frac{k(C)\sigma(C)\gamma(C)n(C)E(C_n)}{\sigma(C_n)\gamma(C_n)n(C_n)E(C)} \qquad (1)$$

Here n is the fractional abundance of the ionic species measured, γ is the electron multiplier gain, σ is the maximum ionization cross section, and $E = I^+(\max)/I^+(\mathrm{obs})$, an empirical factor that corrects the ion current measured at 20 V electron energy to that corresponding to maximum ionization. The E values for C_1–C_5 and the γ values for C, C_2, and C_3 were measured. The electron multiplier gain values for C_4–C_7 were assumed to equal $\gamma(C_3)$. The maximum ionization cross section, $\sigma(C_n)$, was estimated as $0.75[n\sigma(C)]$ using the atomic maximum ionization cross sections for C by Mann.[39] The resulting values (in atm A^{-1} K^{-1}) are $k(C_2) = 0.107$; $k(C_3) = 0.066$; $k(C_4) = 0.052$; $k(C_5) = 0.037$; $k(C_6) = 0.0302$; and $k(C_7) = 0.0262$.

IV. Thermochemical Evaluation of Data

In Figure 1, the log $P(C_n)$ values (in atm), obtained by $P(C_n) = k(C_n)I^+(C_n)T$ from the measured ion currents, are plotted vs $1/T$. These $P(C_n)$ values correspond to the log K_P values for the reaction

$$nC(\mathrm{graph}) = C_n(g) \qquad (2)$$

where n = 1–7. Second law reaction enthalpies and entropies of formation for C_n were obtained from this plot according to the relation $\ln K_P = -\Delta H_T^\circ/RT + \Delta S_T/R$, where T corresponds to the mean of $1/T_{\min}$ and $1/T_{\max}$. The second law values are listed in Table 2 for C_1–C_5.

In the third law method, at each temperature, T, the reaction enthalpy is given by $\Delta H(\theta) = -RT\ln K_P(T) - T\Delta[(G(T) - H(\theta))/T]$, where $K_P(T)$ is the equilibrium constant (or $P(C_n)$) for reaction 2, n = 1–7, and θ is either 0 or 298.15 K, the reference temperature. The second and third law results, $\Delta_rH(C_n,0)$ and $\Delta_rS(C_n,298.15)$, are summarized in Table 3 for C_1–C_5. The individual third law results for $\Delta_rH(C_4,0)$ and $\Delta_rH(C_5,0)$ are listed for each temperature in Tables 4 and 5, respectively. Those for C_6[14] and C_7[15] have been given elsewhere. The thermal functions for C(graph), C(g), and C_2(g) have been taken from Chase et al.,[9] for C_3(g) from Hanson and Pearson,[40] and for C_4(g) and C_5(g) from the present investigation (Table 1). The error terms in Tables 2 and 3 correspond to standard deviations.

Table 2. Second Law Enthalpies, $\Delta_rH(T_{av})$, and Entropies, $\Delta_rS(T_{av})$, of the Reaction $nC(\mathrm{graph}) = C_n(g)$[a]

reaction	no. of data	average T (T range) (K)	$\Delta_rH(T_{av})$ (kJ mol^{-1})	$\Delta_rS(T_{av})$ (J K^{-1} mol^{-1})
C(graph) = C(g)	42	2457 (2185–2806)	720 ± 9	158.2 ± 3.5
2C(graph) = C_2(g)	28	2507 (2266–2806)	793 ± 12	178.7 ± 4.8
3C(graph) = C_3(g)	41	2470 (2185–2841)	764 ± 8	188.8 ± 3.1
4C(graph) = C_4(g)	12	2750 (2665–2891)	1035 ± 46	229 ± 17
5C(graph) = C_5(g)	12	2738 (2642–2841)	1084 ± 71	251 ± 26

[a] Errors correspond to standard deviations.

Table 3. Second and Third Law Enthalpies, $\Delta_rH(0)$, and Entropies, $\Delta_rS(298.15)$, of the Reaction $nC(\mathrm{graph}) = C_n(g)$[a]

	$\Delta_rH(0)$ (kJ mol^{-1})		$\Delta_rS(298.15)$ (J K^{-1} mol^{-1})	
reaction	2nd law	3rd law	2nd law	3rd law
C(graph) = C(g)	716 ± 9	711 ± 5[b]	154.5 ± 3.5	152.4
2C(graph) = C_2(g)	797 ± 12	817 ± 4	172.9 ± 4.8	180.9
3C(graph) = C_3(g)	811 ± 8	831 ± 5	210.9 ± 3.1	218.7
4C(graph) = C_4(g)	1037 ± 46	1052 ± 3	227 ± 17	232.5
5C(graph) = C_5(g)	1096 ± 71	1081 ± 5	254 ± 26	248.6

[a] Uncertainties are the standard deviation. [b] Reference value.

Table 4. Thermochemical Equilibrium between Graphite and C_4(g): 4C(graph) = C_4(g) and Its Evaluation by the Third Law Method

T (K)	exptl ion current (A) $I(^{48}C_4^+)$	log $K_P(T)$	$-\Delta[G(T) - H(0)/T]$ (J K^{-1} mol^{-1})	$\Delta_fH(0)$[a] (kJ mol^{-1})
2665	3.84×10^{-11}	−8.2746	235.18	1048.9
2699	6.00×10^{-11}	−8.1080	235.17	1053.7
2732	1.10×10^{-10}	−7.8076	235.16	1050.8
2733	9.56×10^{-11}	−7.8677	235.16	1054.4
2770	2.21×10^{-10}	−7.4971	235.15	1049.0
2784	2.90×10^{-10}	−7.3778	235.15	1047.9
2806	3.74×10^{-10}	−7.2640	235.14	1050.0
2672	3.64×10^{-11}	−8.2971	235.18	1052.8
2724	8.07×10^{-11}	−7.9427	235.16	1054.8
2754	1.33×10^{-10}	−7.7197	235.15	1054.6
2785	2.17×10^{-10}	−7.5033	235.15	1055.0
2841	4.95×10^{-10}	−7.1368	235.14	1056.2

[a] Average, 1052.3 ± 2.9. Uncertainty is the standard deviation.

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Table 5. Thermochemical Equilibrium between Graphite and C_5(g): 5C(graph) = C_5(g) and Its Evaluation by the Third Law Method

T (K)	exptl ion current (A) $I(^{60}C_5^+)$	log $K_P(T)$	$-\Delta[G(T) - H(0)/T]$ (J K^{-1} mol^{-1})	$\Delta_fH(0)^a$ (kJ mol^{-1})
2665	9.81×10^{-11}	−8.0131	249.91	1074.8
2699	1.51×10^{-10}	−7.8622	249.85	1080.6
2732	2.67×10^{-10}	−7.5674	249.80	1078.3
2770	5.75×10^{-10}	−7.2284	249.74	1075.1
2784	7.83×10^{-10}	−7.0922	249.72	1073.2
2806	8.98×10^{-10}	−7.0294	249.68	1078.2
2642	3.67×10^{-11}	−8.4443	249.95	1087.5
2672	8.00×10^{-11}	−8.1010	249.90	1082.1
2724	1.72×10^{-10}	−7.7606	249.81	1085.2
2754	2.97×10^{-10}	−7.5186	249.76	1084.3
2785	4.47×10^{-10}	−7.3359	249.71	1086.6
2841	1.12×10^{-9}	−6.9292	249.63	1086.1

[a] Average, 1081.0 ± 5.0. Uncertainty is the standard deviation.

Table 6. Enthalpies of Formation, $\Delta_fH(C_n,g,0)$, Atomization Enthalpies, $\Delta_aH(C_n,g,0)$, and Fragmentation Energies, $\Delta_aH(C_n,g,0) - \Delta_aH(C_{n-1},g,0)$, for C_2–C_7 (in kJ mol^{-1})[a]

molecule	$\Delta_fH(C_n,g,0)$	$\Delta_aH(C_n,g,0)$	$\Delta_aH(C_n,g,0) - \Delta_aH(C_{n-1},g,0)$
C_2	817 ± 8	605 ± 8	605
C_3	831 ± 13	1303 ± 13	698
C_4	1052 ± 16	1793 ± 17	490
C_5	1081 ± 16	2475 ± 17	682
C_6	1312 ± 18	2955 ± 20	480
C_7	1325 ± 18	3653 ± 20	698

[a] Uncertainties include all estimated sources of error such as the thermal functions, temperature measurements, and standard deviations.

In Table 6, we list the selected enthalpies of formation together with the enthalpies of atomization or binding energies, $\Delta_aH(C_n,g,0)$, corresponding to the reaction

$$C_n(g) = nC(g) \tag{3}$$

These values are based on the average third law enthalpies of formation, $\Delta_fH(C_n,g,0)$, and in Table 3 and the enthalpy of formation (in kJ mol^{-1}) of C(g), $\Delta_fH(C,g,0) = 711.19 \pm 0.46$.[9] Here the error terms correspond to overall errors. For C_4–C_7, the short temperature range of measurements, the small signals of ion currents measured, and the comparatively large scatter of data did not permit us to obtain reliable second law enthalpies. Inspection of Table 3 shows that for C_2 and C_3 the second law values agree with the corresponding third law values, taking the overall error of the second law values as twice the standard deviation.

Also listed in Table 6 are the incremental binding energies or fragmentation energies, $\Delta_aH(C_n,g,0) - \Delta_aH(C_{n-1},g,0)$, for n = 2–7. As can be seen, the odd-numbered clusters are more stable toward the loss of a carbon atom than the adjacent even-numbered clusters. A similar trend has also been measured for the fragmentation energies of the corresponding cluster ions C_n^+ [41] and predicted from ab initio calculations for both C_n and C_n^+.[11]

V. Comparison with Literature Data

In Table 7, we compare our results for the enthalpies of formation of the C_2–C_5 molecules with other experimental and theoretical literature data, some of them from reviews.[8–13,42–44] Our main emphasis in the present investigation has been on carbon clusters, C_n, n = 4–7. For C_4 and C_5, most of the previous experimental information comes from Drowart et al.[8] These authors also give lower limits for $\Delta_fH(C_n(g),0)$ of 1172 kJ mol^{-1} for C_6 and 1130 kJ mol^{-1} for C_7, consistent with our present results (see Table 6).

Table 7. Comparison of Values from This Work and Literature Values of the Enthalpy of Formation of Small Carbon Clusters, $\Delta_fH(C_n,g,0)$, in kJ mol^{-1}

	molecule				
method	C_2	C_3	C_4	C_5	ref
KCMS[a]	817 ± 8	831 ± 13	1052 ± 16	1081 ± 16	this work
KCMS[b]	797 ± 24	811 ± 16			this work
KCMS[a]	828 ± 7	787 ± 10	1006 ± 28	1006 ± 28	8
KCMS[b]	819 ± 7	781 ± 6	960 ± 30	973 ± 22	8
review	829 ± 4	820 ± 17	971 ± 33	979 ± 25	9
review	822 ± 10	831 ± 13	1025 ± 50	1040 ± 60	10
theoretical (scaled)	805	792	1009	1019	11
experimental[c]			1045	1060	12,13
theoretical			1069 ± 42		42
theoretical	823 ± 9				43
review	823 ± 9				44
spectroscopic	815 ± 2				46

[a] Knudsen cell mass spectrometry; reported third law values. [b] Second law values (for the present investigation, the error term corresponds to twice the standard deviation.) [c] Third law data by Drowart et al.,[8] reevaluated by Martin et al.[12,13]

Previous knowledge of the thermodynamic properties of the molecules C_2–C_5 has been reviewed mainly by Chase et al.[9] and Glushko et al.[10] For C_4 and C_5, both reviews interpret the results by Drowart et al. using different estimated thermal functions. Chase et al. used the second law results by Drowart et al. as their basis, whereas Glushko et al.[10] took both second and third law results into account. In addition, they used for C_4 other mass spectrometric equilibrium results by Zavitsanos and Carlson,[45] who measured a single data point at 3003 K, reporting a value for $\Delta_fH(C_4,g,298.15)$ of 1015 kJ mol^{-1}. A second law value of $\Delta_fH(C_4,g,0)$ is reported by Steele and Bourgelas[25] as 961 kJ mol^{-1}, similar to that obtained by Drowart et al.[8] (see Table 7).

The assessment by Glushko et al.[10] of the data for C_4 and C_5 by Drowart et al. yields $\Delta_fH(0)$ values in much better agreement with the present results than those by Chase et al.[9] Very recently, Martin et al.[12,13] also reevaluated the third law data by Drowart et al. for C_4 and C_5, resulting in $\Delta_fH(0)$ values that are in good agreement with our present results. Martin et al. have based their thermal functions calculation on the harmonic frequencies taken from the most accurate ab initio work available. For C_4 they have considered in their evaluation both the rhombic and the linear structure but noted that the resulting thermal functions are quite close to those obtained by considering the linear form only. Our thermal functions, presented in Table 1, are similar to those calculated by Martin et al. In our calculations, new experimental results for harmonic frequencies have been considered that were not yet available to Martin et al.

For C_2, our $\Delta_fH(0)$ value is in excellent agreement with the most recent spectroscopic value by Urdahl et al.[46] This value is lower than the one chosen by Chase et al.[9] based solely on earlier spectroscopic results by Messerle and Krauss.[47] Huber and Herzberg[44] had noted that the spectroscopic value by Messerle and Krauss was somewhat doubtful and had based their assessment also on mass spectrometric results. For C_3, our present third law results are in good agreement with the assessed value by Glushko et al.[10] These authors have based their selected value on the third

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law values of several mass spectrometric results[8,45,48-50] using thermal functions for gaseous C_3 that were very similar to those used by Hansen and Pearson[40] and by Strauss and Thiele.[51] Chase et al.[9] based their assessment mainly on the second law results by Drowart et al.[8] and calculated their thermal functions for C_3 to best fit these second law data.

VI. Comparison of Experimental and Theoretical Results

Raghavachari and Binkley[11] have calculated the binding energies (or atomization enthalpies) of gaseous C_2–C_{10} using both Möller–Plesset perturbation theory and coupled cluster theory; a 6-31G* basis set was used. We have found that our experimental results (Table 6) exceed the CCD+ST(CCD)/6-31G* values by a factor of 1.071 ± 0.008, where the uncertainty is the standard deviation. This scaling factor is a little smaller than the factor of 1.1 selected by Raghavachari and Binkley and is close to the value (1.082) reported by Martin et al.[13] Based on the predictions by Raghavachari and Binkley[11] and our scaling factor of 1.071, the predicted atomization energies of C_8, C_9, and C_{10} become 43.16, 49.77, and 57.75 eV, respectively.

Watts et al.[42] recently calculated the atomization energy of C_4 by coupled cluster methods without using any correction terms. Their $\Delta_aH(0)$ value, at the CCSD(T)/PVQZ level, of 1812 ± 42 kJ mol^{-1} is in good agreement with our experimental value of 1793 ± 17 kJ mol^{-1}.

VII. Conclusion

New thermal functions, have been calculated for gaseous C_4 and C_5. The thermal functions for C_2–C_5 have been used with new equilibrium partial pressures in the evaluation of enthalpies of formation $\Delta_fH(C_n,g,0)$ of 817 ± 8 (C_2), 831 ± 13 (C_3), 1052 ± 16 (C_4), and 1081 ± 16 (C_5) kJ mol^{-1}. The corresponding atomization enthalpies $\Delta_aH(C_n,g,0)$ are calculated as: 605 ± 8 (C_2), 1303 ± 13 (C_3), 1793 ± 17 (C_4), and 2475 ± 17 (C_5) kJ mol^{-1}. The enthalpies of formation for C_4 and C_5, reported here, are higher than previously believed[9,10] but are in good agreement with theoretical predictions.[11-13,42]

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