The enthalpy of sublimation of diphenylacetylene from Knudsen effusion studies

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Abstract

The enthalpy of sublimation of diphenylacetylene at 298.15 K, $\Delta_{cr}^{g}H_{m}^{\ominus}(C_2(C_6H_5)_2]$ = 95.1 ± 1.1 kJ mol^{-1}, was derived from vapour pressure–temperature data, obtained with two different Knudsen effusion apparatus, and from heat capacity measurements obtained by differential scanning calorimetry. The molybdenum–diphenylacetylene bond dissociation enthalpy in $Mo(\eta^5\text{-}C_5H_5)_2[C_2(C_6H_5)_2]$ was reevaluated as 115 ± 26 kJ mol^{-1}, on the basis of the new value for $\Delta_{cr}^{g}H_{m}^{\ominus}[C_2(C_6H_5)_2]$.

INTRODUCTION

The enthalpy of sublimation of diphenylacetylene has received considerable attention in recent years, in relation to the stabilization energies of phenylalkynes [1], to the strain energy of 2,3-diphenylcycloprop-2-en-1-one [2], to the energetics of the molybdenum–diphenylacetylene bond [3], and to a method of estimation of enthalpies of sublimination of hydrocarbons [4].

In 1938, Wolf and Weghofer, using a Knudsen torsion-effusion apparatus, obtained $\Delta_{cr}^{g}H_{m}^{\ominus}[C_2(C_6H_5)_2] = 88.7 \pm 1.2$ kJ mol^{-1} at the mean temperature of the experiments, $T_m = 317$ K [5]. More recently, head space analysis measurements led to $\Delta_{cr}^{g}H_{m}^{\ominus}[C_2(C_6H_5)_2] = 90.4 \pm 4.6$ kJ mol^{-1} at $T_m = 310$ K [2, 6]. Early experiments using the Knudsen effusion method in the Lisbon laboratory, however, gave a considerably higher value for the enthalpy of sublimation of diphenylacetylene (99.9 ± 1.5 kJ mol^{-1}, $T_m = 299.11$ K [3, 7]). This discrepancy led us to redetermine the enthalpy

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of sublimination of diphenylacetylene using two different Knudsen effusion apparatus, in order to improve the accuracy of our previously reported value for the molybdenum–diphenylacetylene bond dissociation enthalpy [3].

EXPERIMENTAL

The diphenylacetylene (Aldrich, 99%) used in the Knudsen effusion experiments was sublimed twice prior to use. No phase transitions other than melting were detected in the temperature range 253.15–343.15 K, using a Setaram DSC 121 at a heating rate of 5 K min^{-1}. The onset and the maximum temperature of the melting peak were 331.5 ± 0.2 and 334.4 ± 0.6 K, respectively. The uncertainties quoted are the standard deviations of the mean of two determinations.

The above sample and a non-sublimed sample of the same batch (temperature of melting = 331.51 ± 0.01 K, average of three determinations) were used in the measurements of heat capacity and enthalpy of melting by DSC. The heating rates were 2 and 5 K min^{-1} in the heat capacity and in the enthalpy of melting experiments, respectively.

The Lisbon Knudsen effusion apparatus (Fig. 1) is a modified version of the one previously described, and the same operating procedure was followed in this work [8]. The design and dimensions of the bronze cell 1 have been retained. The effusion hole was drilled in 2.09 × 10^{-3} cm-thick copper foil (Cu 99%, Goodfellow Metals) soldered to the cell lid and was 4.40 × 10^{-3} cm^2 in area (hole 1). The cell fits tightly in a cylindrical brass block (2) at the base of the vacuum chamber (3). The brass vacuum chamber is closed at the top by a brass lid (4) and a Viton O-ring. The
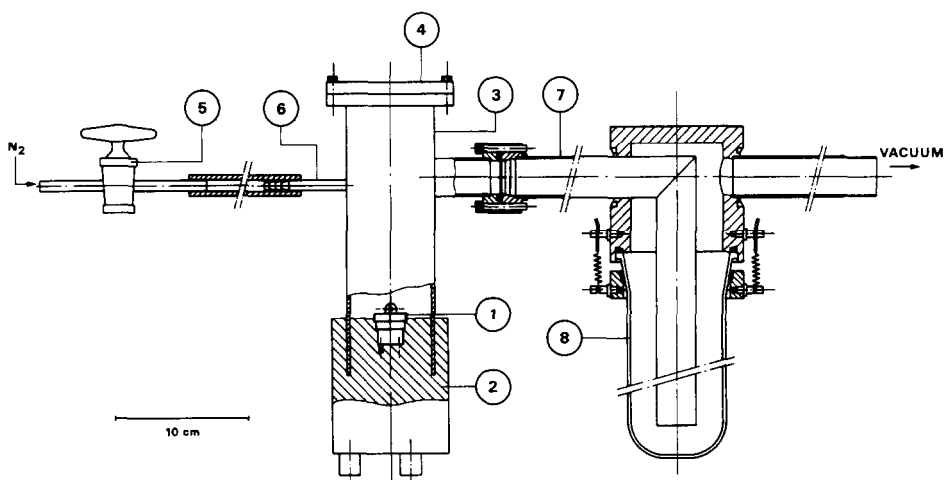

Fig. 1. Knudsen effusion apparatus: (1) cell, (2) brass block, (3) brass vacuum chamber, (4) brass lid, (5) glass tap, (6) inlet, (7) steel vacuum line, (8) glass trap.

vacuum chamber can be filled with nitrogen (which is faster to pump off than air, and ensures an inert atmosphere when studying air-sensitive compounds [9]) through the glass tap (5), connected by a small neoprene tube to inlet (6). The vacuum chamber is connected to a steel vacuum line, (7) which includes a glass trap, (8) immersed in liquid nitrogen. The high vacuum pumping system, consisting of an Edwards ES200 rotary pump and an Edwards E04 diffusion pump with a liquid nitrogen trap, was as before [8]. The brass block (2) was immersed in a water bath whose temperature is controlled to ± 0.01 K with a Haake ED Unitherm thermostat and measured with identical precision with a calibrated mercury thermometer. The mass loss from the sample was determined by weighing the cell to $\pm 10^{-5}$ g with a Sartorius 2474 balance. Tests of the reliability of this apparatus have already been reported [9].

The Porto Knudsen effusion apparatus, procedure, and tests have been described before [10]. This apparatus enables the simultaneous operation of three Knudsen cells. In the present work the effusion holes had a thickness of 4.9×10^{-3} cm, and the areas were 5.96×10^{-3} cm^2 (hole 2), 8.13×10^{-3} cm^2 (hole 3), and 8.62×10^{-3} cm^2 (hole 4), respectively. The cells were immersed in a water bath controlled to ± 0.001 K with a Tronac PTC 40 thermostat. The temperature was measured to ± 0.01 K with a calibrated mercury thermometer. In each effusion experiment, the mass loss was measured by weighing the cell to $\pm 10^{-5}$ g with a Mettler H54 balance.

The vapour pressures p of the samples were calculated from

$$p = \frac{m}{A t K_c} \left(\frac{2 \pi R T}{M} \right)^{1/2} \tag{1}$$

$$K_c = \frac{8r}{3L + 8r} \tag{2}$$

where m is the mass loss during the time t, A is the area of the effusion hole, M is the molar mass of the vapour, R is the gas constant, T is the absolute temperature, and K_c is the Clausing factor [11]. K_c is calculated from eqn. (2), where L and r are the thickness and the radius of the effusion hole, respectively [11].

RESULTS AND DISCUSSION

Five independent determinations of the average heat capacity of diphenylacetylene, in the temperature range 298.15–323.15 K gave the result $C_{p,m}^{\ominus}(\text{cr}) = 240.3 \pm 2.9$ J mol^{-1} K^{-1}. The enthalpy of melting of diphenylacetylene, $\Delta_{cr}^{l} H_m^{\ominus} = 20.0 \pm 0.1$ kJ mol^{-1} at 331.5 K, was also obtained from the results of five independent experiments. The uncertainties quoted for $C_{p,m}^{\ominus}(\text{cr})$ and $\Delta_{cr}^{l} H_m^{\ominus}$ are twice the standard deviation of the mean.

TABLE 1

Experimental results and residuals of eqn. (3)

T/K	p/Pa				$100 \times \Delta \ln p$			
	Hole 1	Hole 2	Hole 3	Hole 4	Hole 1	Hole 2	Hole 3	Hole 4
298.273		0.1053	0.1077	0.1038		−1.23	2.58	1.20
300.05	0.12425				−0.56			
300.61	0.13440				0.22			
301.218		0.1596	0.1518	0.1506		2.65	2.21	2.25
301.45	0.15128				1.49			
302.34	0.16538				−0.73			
303.44	0.19177				0.43			
304.190		0.2249	0.2181	0.2164		−1.06	−0.68	−0.55
304.29	0.21021				−0.87			
306.205		0.2814	0.2733	0.2743		3.21	−0.27	0.81
306.22	0.26478				−1.38			
307.06	0.30023				1.01			
307.97	0.33297				0.40			
308.200		0.3570	0.3561	0.3459		−1.32	−2.76	−1.19
310.160		0.4522	0.4474	0.4450		−1.48	−0.27	−2.23
313.198		0.6413	0.6421	0.6390		0.78	−0.80	−0.09
316.153		0.9379	0.9208	0.9220		−1.55	−0.02	−0.21

The vapour pressure–temperature data shown in Table 1 were fitted to eqn. (3)

$$\ln(p/Pa) = a + \frac{b}{(T/K)} \tag{3}$$

by the least-squares method; the residuals are also presented in this table. The values obtained for the constants a and b, where $b = -\Delta_{cr}^{g} H_m^{\ominus}/R$, are shown in Table 2, together with the values derived for the enthalpies of

TABLE 2

Parameters a and b of eqn. (3) and values of the enthalpy of sublimation of diphenylacetylene

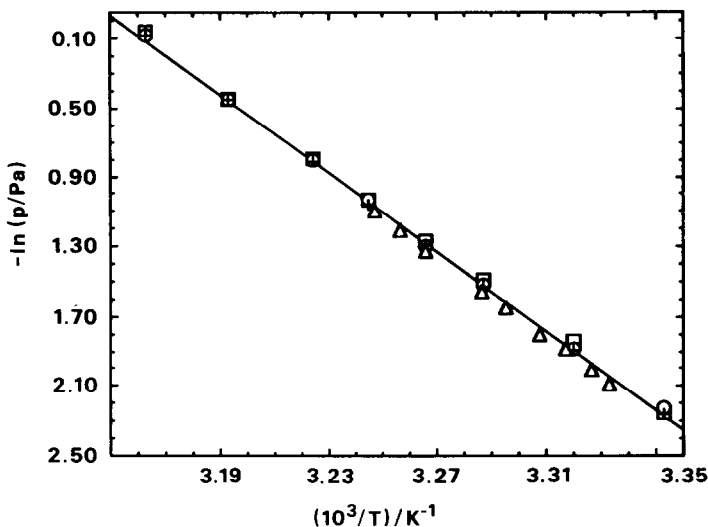| Hole	T_m/K	a	b	$\Delta_{cr}^{g} H_m^{\ominus}(T_m)$ /kJ mol^{-1}	$\Delta_{cr}^{g} H_m^{\ominus}(298.15\ K)$ /kJ mol^{-1}
1 (Lisbon)	303.71	35.870 ± 0.899	11389 ± 272	94.7 ± 2.3	95.0 ± 2.3
2 (Porto)	307.21	35.743 ± 1.003	11329 ± 308	94.2 ± 2.6	94.7 ± 2.6
3 (Porto)	307.21	35.755 ± 0.874	11337 ± 269	94.3 ± 2.2	94.8 ± 2.2
4 (Porto)	307.21	36.157 ± 0.719	11464 ± 220	95.3 ± 1.8	95.8 ± 1.8
Mean		35.881 ± 0.440	11380 ± 135		95.1 ± 1.1

Fig. 2. Plot of $\ln(p/\text{Pa})$ against $1/T$: $\triangle$, hole 1; $\square$, hole 2; $\bigcirc$, hole 3; $+$, hole 4.

sublimation. The uncertainties quoted for a, b, and the $\Delta_{cr}^g H_m^{\ominus}$ values include the student's factor for 95% confidence level. The plot of $\ln(p/Pa)$ versus $1/T$ for the experimental results is presented in Fig. 2. The sublimation enthalpies at 298.15 K were derived from the sublimation enthalpies at the mean temperature T_m of the experiments (eqn. (4))

$$\Delta_{cr}^g H_m^{\ominus}(298.15 \text{ K}) = \Delta_{cr}^g H_m^{\ominus}(T_m) + \Delta_{cr}^g C_{p,m}^{\ominus}(298.15 - T_m) \tag{4}$$

The value $\Delta_{cr}^g C_{p,m}^{\ominus} = -53.2 \text{ J mol}^{-1} \text{ K}^{-1}$ was calculated from the heat capacity of the gas at 300 K (187.1 J mol^{-1} K^{-1}), estimated by Benson's scheme [12], and from the heat capacity of the solid in the temperature range 298.15–323.15 K (240.3 J mol^{-1} K^{-1}) measured in this work.

Equation (1) is based on the assumption of free molecular flow for the effusion of the vapour through the cell hole. This assumption holds when the ratio r/λ is close to zero, where r is the hole radius and λ the mean free path of the molecules inside the cell. Hiby and Pahl [13] and Carman [14] suggested that when r/λ is not zero, eqn. (1) should be multiplied by $(1 + 0.24r/\lambda)^{-1}$. The value of λ is given by

$$\lambda = \frac{kT}{\sqrt{2}\,\pi\sigma^2 p} \tag{5}$$

where k is the Boltzmann constant, T the absolute temperature, p the pressure, and σ the collision diameter of the gaseous species. The Hiby and Pahl correction is, therefore, pressure dependent, and its inclusion in eqn. (1) may alter the slope of the vapour pressure–temperature plot and give a different value for the enthalpy of sublimation [15]. To test the influence of the Hiby and Pahl correction in our results, the collision diameter of

TABLE 3

p and T values from the vapour pressure equation (mean values of the four holes)

p/Pa	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T/K	298.03	303.54	306.86	309.26	311.15	312.71	314.04	315.20	316.23

diphenylacetylene, $\sigma = 500$ pm, was estimated from projections of its molecular structure [16], including the van der Waals radii [17], in the x, y, and z planes. Accounting for the Hiby and Pahl factor in the experiment with the highest r/λ ratio ($A = 8.62 \times 10^{-3}$ cm^2) leads to a decrease of 1.0 kJ mol^{-1} in the corresponding $\Delta_{cr}^g H_m^\ominus(T_m)$. For the lowest r/λ ratio in our experiments ($A = 4.40 \times 10^{-3}$ cm^2), the decrease is only 0.4 kJ mol^{-1}. Therefore, in these cases, the Hiby and Pahl correction is within the experimental error of the measurements.

The agreement between the vapour pressure–temperature data obtained with four different holes indicates that a self-cooling effect [15] did not occur in these experiments.

Table 3 lists the (p, T) values calculated from eqn. (3) (where a and b are the mean values in Table 2), within the experimental range of pressures used, 0.1–0.9 Pa.

The mean value of the enthalpies of sublimation of diphenylacetylene at 298.15 K in Table 2 is 95.1 ± 1.1 kJ mol^{-1}. This value is compared in Table 4 with other results of $\Delta_{cr}^g H_m^\ominus[C_2(C_6H_5)_2]$ published in the literature and corrected to 298.15 K using the $\Delta_{cr}^g C_{p,m}^\ominus$ value quoted above (-53.2 J mol^{-1} K^{-1}). It should be noted that the head space analysis method usually gives results that are lower by $\leqslant 5\%$ that the recommended values in the literature [6]. In this case, the difference relative to the value proposed in the present work (4.1 kJ mol^{-1}) is within those limits and both values agree within the quoted error bars. Using $\Delta_f H_m^\ominus[C_2(C_6H_5)_2, cr] = 312.4 \pm 1.1$ kJ mol^{-1} [18], the standard enthalpy of formation of gaseous diphenylacetylene is derived as $\Delta_f H_m^\ominus[C_2(C_6H_5)_2, g] = 407.5 \pm 1.6$ kJ mol^{-1}.

The molybdenum–diphenylacetylene bond dissociation enthalpy, $D[Mo–C_2(C_6H_5)_2]$, in $Mo(Cp)_2[C_2(C_6H_5)_2]$ ($Cp = \eta^5$–C_5H_5) can be reevalu-

TABLE 4

Enthalpies of sublimation of diphenylacetylene at 298.15 K

Method	$\Delta_{cr}^g H_m^\ominus(298.15$ K)/kJ mol^{-1}	Ref.
Torsion effusion	89.7 ± 1.2	5
Head space analysis	91.0 ± 4.6	2, 6
Knudsen effusion	95.1 ± 1.1	This work

ated by considering reaction (6) and eqn. (7)

$$Mo(Cp)_2[C_2(C_6H_5)_2](g) + 2Cl(g) \xrightarrow{\Delta_r H_m^{\ominus}} Mo(Cp)_2Cl_2(g) + C_2(C_6H_5)_2(g) \qquad (6)$$
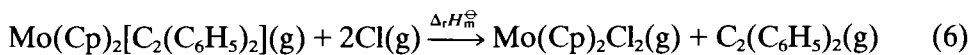
$$\Delta_r H_m^{\ominus} = D[Mo-C_2(C_6H_5)_2] - 2\bar{D}(Mo-Cl) \qquad (7)$$

where $\bar{D}(Mo-Cl)$ is the mean bond dissociation enthalpy in $Mo(Cp)_2Cl_2$. Using $\Delta_f H_m^{\ominus}[Mo(Cp)_2(C_2(C_6H_5)_2), g] = 661 \pm 22 \text{ kJ mol}^{-1}$ [3], $\Delta_f H_m^{\ominus}[Mo-(Cp)_2Cl_2, g] = 4.6 \pm 4.9 \text{ kJ mol}^{-1}$ [19], $\Delta_f H_m^{\ominus}[Cl, g] = 121.679 \text{ kJ mol}^{-1}$ [20], and the estimated value for $\bar{D}(Mo-Cl) = 303.8 \pm 7.1 \text{ kJ mol}^{-1}$ [19] a value of $D[Mo-C_2(C_6H_5)_2] = 115 \pm 26 \text{ kJ mol}^{-1}$ is obtained

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