



## Standard enthalpies of formation of phenanthrene and naphthacene<sup>a</sup>

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Standard enthalpies of combustion of phenanthrene and naphthacene were determined to be  $-(7048.7 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$  and  $-(9005.1 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, by means of high-precision micro-combustion calorimetry. The former result agrees very well with that reported by Steele *et al.* (*AIChE Symposium Series 279*, **1990**, 86, 138–154). The latter confirms theoretical predictions. By using standard enthalpies of sublimation from the literature, the standard molar enthalpies of formation of phenanthrene and naphthacene in the gas phase were derived to be  $(201.7 \pm 2.9) \text{ kJ} \cdot \text{mol}^{-1}$  and  $(331.6 \pm 4.4) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. The enthalpy of the rearrangement reaction from anthracene to phenanthrene was evaluated to be  $-(28.4 \pm 4.1) \text{ kJ} \cdot \text{mol}^{-1}$ . © 2002 Elsevier Science Ltd. All rights reserved.

**KEYWORDS:** micro-combustion calorimetry; phenanthrene; naphthacene; standard enthalpy of formation

### 1. Introduction

Formation of polycyclic aromatic hydrocarbons (PAHs) has been attracting attention from many viewpoints which include interstellar chemistry,<sup>(1)</sup> geochemistry especially in relation to the origin of petroleum,<sup>(2)</sup> and environmental chemistry.<sup>(3)</sup> Obviously, the standard enthalpy of formation gives a thermodynamic basis for these advanced studies. This quantity has been determined mainly by means of high-precision combustion calorimetry and sublimation calorimetry. Surprisingly, however, those values have been confirmed only for a very few PAHs.

In 1990, Steele *et al.*<sup>(4)</sup> reported the enthalpy of combustion of phenanthrene which differs beyond the error intervals from that reported by Coleman and Pilcher in 1966.<sup>(5)</sup> Theoretical studies<sup>(6,7)</sup> have suggested that the calorimetric value of the enthalpy of formation of naphthacene (tetracene) is incorrect. Combustion calorimetry of pentacene has not been reported yet. In order to support thermodynamic aspects of the current studies

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where interest is heading to the larger PAHs, it is desirable to confirm the thermodynamic quantities of these smaller PAHs.

Very recently, the author developed a high-precision micro-combustion calorimeter in which the combustion energy can be determined not only with a few milligrams of sample for one experiment but also as precisely as in conventional macro-combustion calorimetry.<sup>(8,9)</sup> In the present study, high-precision micro-combustion calorimetry of phenanthrene and naphthacene was carried out, and standard enthalpies of formation were determined.

## 2. Experimental

Phenanthrene (zone-refined) and naphthacene (mass fraction > 0.99) were purchased from Tokyo Chemical Industry Co., Ltd. The mass-fraction of phenanthrene was determined to be 0.9999 by means of d.s.c. (Perkin Elmer, DSC7). It is difficult to determine the purity of naphthacene by d.s.c. or <sup>1</sup>H-n.m.r., because of the high melting temperature and the low solubility. The purity of naphthacene was not determined. The samples were used for calorimetry without further purification.

A high-precision micro-combustion calorimeter, which the author has recently developed, was used under isoperibol conditions. Details of the combustion calorimetry were described elsewhere.<sup>(9)</sup> A pellet of mass 3.2 mg and diameter 1.6 mm was loaded on a square platinum boat of dimensions 3 mm on a side, and 0.1 mm in thickness. The pellet was fastened on the boat by a platinum wire of 0.03 mm diameter. Petroleum jelly of mass (0.03 to 0.06) mg was pasted on the pellet in order to obtain ignition. The sample and petroleum jelly were precisely weighed on an ultra-microbalance (Sartorius, 4504MP8), the certified standard deviation of which is 0.2  $\mu$ g. The boat was hung under a platinum shield at the center of the bomb. The bomb, of 9.8 cm<sup>3</sup> internal volume, was filled with high-purity oxygen gas to a pressure of 4.0 MPa. Water (10 mm<sup>3</sup>) was placed in the bomb to saturate the gas. Calorimetric temperatures were measured every 2 s by using a thermistor attached to the bomb holder. The change in the resistance of the thermistor was recorded as the off-balance of the d.c. voltage in a Wheatstone bridge.

The energy equivalent of the calorimeter and the standard deviation of the mean were determined to be  $(67.824 \pm 0.003) \text{ J} \cdot \text{K}^{-1}$  by burning masses of  $\approx 4.9$  mg (5 experiments) of thermochemical standard benzoic acid (NIST SRM 39i,  $\Delta_{\text{c}}u = -26434 \text{ J} \cdot \text{g}^{-1}$  under certificate conditions). The standard massic energy of combustion of petroleum jelly was determined to be  $-(46.166 \pm 0.018) \text{ kJ} \cdot \text{g}^{-1}$  in separate experiments.<sup>(8)</sup> Nitric acid in the bomb solution was determined by u.v. absorbance at  $\lambda = 201 \text{ nm}$  ( $\lg \varepsilon = 3.98$ ). The calculation of the energy equivalent and reduction to standard states at  $T = 298.15 \text{ K}$  and  $p = 0.1 \text{ MPa}$  were carried out by the literature method<sup>(10)</sup> and with thermochemical values compiled in the literature.<sup>(11,12)</sup> The recommended standard massic energy of combustion of benzoic acid,  $-26.414 \text{ kJ} \cdot \text{g}^{-1}$ ,<sup>(13,14)</sup> was used to determine the energy equivalent. The uncertainties (random errors) of the derived quantities were evaluated by the literature method.<sup>(15)</sup> The decomposition energy of  $\text{HNO}_3$ ,  $\Delta_{\text{dec}}U_{\text{m}} = 59.7 \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(12)</sup> was used in the reduction to ideal combustion reactions.

TABLE 1. Auxiliary quantities for the calculation of standard energies of combustion<sup>a</sup>

Materials	Formula	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$M/(\text{g} \cdot \text{mol}^{-1})$	$c_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})$	$(\partial u/\partial p)_T/(\text{J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1})$
Phenanthrene	$\text{C}_{14}\text{H}_{10}$	1.18 <sup>(4)</sup>	178.233	1.236 <sup>(4)</sup>	(-0.053)
Naphthacene	$\text{C}_{18}\text{H}_{12}$	1.29 <sup>(17)</sup>	228.293	1.036 <sup>(22)</sup>	(-0.053)
Benzoic acid	$\text{C}_7\text{H}_6\text{O}_2$	1.32 <sup>b</sup>	122.123	1.21 <sup>(13)</sup>	(-0.053)
Petroleum jelly	$\text{CH}_{1.953}$ <sup>(8)</sup>	0.9 <sup>(8)</sup>	13.979	(2.21)	(-0.293)

<sup>a</sup> Values in parentheses are estimated. <sup>b</sup> Certificate of analysis (NIST SRM 39i).

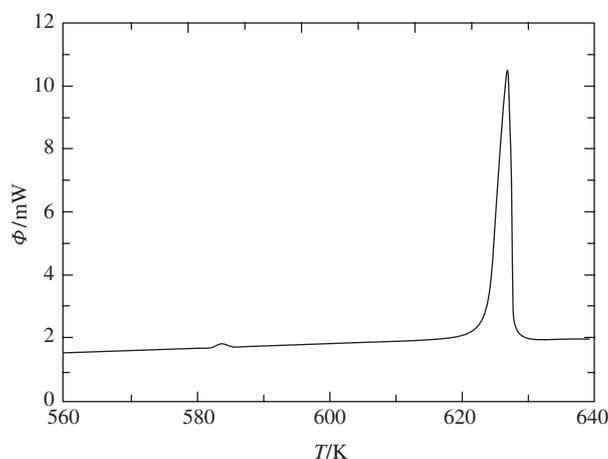


FIGURE 1. A d.s.c. thermogram of naphthacene at a heating rate of  $0.333 \text{ K} \cdot \text{s}^{-1}$ . Plot of heat flow  $\Phi$  against temperature  $T$ . Sample was sealed in an aluminum pan under He gas flow.

### 3. Results

Table 1 lists the auxiliary quantities used in the calculations. Tables 2 and 3 summarize the results of the combustion calorimetry of phenanthrene and naphthacene, respectively. The experiments on naphthacene often suffered from the formation of soot. In such cases, the amount of soot was determined by weighing it on the platinum boat after a combustion experiment. The massic energy of combustion of the soot was assumed to be  $33 \text{ kJ} \cdot \text{g}^{-1}$ , the same as that of graphite.<sup>(11)</sup>

Figure 1 shows a d.s.c. thermogram of naphthacene. Naphthacene of mass 0.398 mg was sealed in an aluminum pan under helium gas flow. A melting peak that corresponded to  $\Delta_{\text{fus}}H_{\text{m}} = 35.9 \text{ kJ} \cdot \text{mol}^{-1}$  was observed at  $T_{\text{fus}} = 623.2 \text{ K}$ , while  $T_{\text{fus}} = 630 \text{ K}$  was reported by Wakayama and Inokuchi.<sup>(16)</sup> Another small peak that corresponded to  $\Delta_{\text{trs}}H_{\text{m}} = 1.0 \text{ kJ} \cdot \text{mol}^{-1}$  was found at  $T = 581.4 \text{ K}$ . Crystallographic data indicate that naphthacene and pentacene belong to the  $\text{P}\bar{1}$  space group at room temperature, while

TABLE 2. Summary of combustion calorimetric results for phenanthrene.  $m$ , mass of phenanthrene;  $m$  (Vas), mass of petroleum jelly;  $n$  ( $\text{HNO}_3$ ), amount of  $\text{HNO}_3$ ;  $\varepsilon^i$ , energy equivalent of the bomb contents in the initial state;  $\varepsilon^f$ , energy equivalent of the bomb contents in the final state;  $T_i$ , initial temperature of the reaction period;  $T_f$ , final temperature of the reaction period;  $\Delta T_c$ , correction to temperature rise;  $\Delta T_{\text{ad}}$ , adiabatic temperature rise;  $\Delta U_{\text{ign}}$ , ignition energy;  $-\Delta_{\text{IBP}}U$ , energy of isothermal bomb process;  $\Delta U(\text{HNO}_3)$ , decomposition energy of  $\text{HNO}_3$ ;  $\Delta U_{\Sigma}$ , the correction to standard states;  $\Delta_c u^0$ , standard massic energy of combustion;  $\Delta_c U_{\text{m}}^0$ , standard molar energy of combustion

Expt. no.	1	2	3	4
$m/\text{mg}$	3.2341	3.2245	3.2098	3.2218
$m(\text{Vas})/\text{mg}$	0.0469	0.0431	0.0484	0.0276
$n(\text{HNO}_3)/\mu\text{mol}$	0.065	0.048	0.046	0.044
$\varepsilon^i/(\text{J} \cdot \text{K}^{-1})$	0.427	0.427	0.426	0.426
$\varepsilon^f/(\text{J} \cdot \text{K}^{-1})$	0.432	0.431	0.430	0.430
$(T_i/\text{K}) - 273.15$	23.61031	23.61161	23.61083	23.60919
$(T_f/\text{K}) - 273.15$	25.528459	25.523943	25.519183	25.509845
$\Delta T_c/\text{K}$	0.012062	0.013969	0.014812	0.014557
$\Delta T_{\text{ad}}/\text{K}$	1.90609	1.89837	1.89354	1.88610
$\Delta U_{\text{ign}}/\text{J}$	0.056	0.095	0.083	0.062
$-\Delta_{\text{IBP}}U/\text{J}$	130.040	129.473	129.154	128.667
$\Delta U(\text{HNO}_3)/\text{J}$	0.004	0.003	0.003	0.003
$\Delta U_{\Sigma}/\text{J}$	0.084	0.084	0.083	0.084
$-\Delta_c u^0/(\text{kJ} \cdot \text{g}^{-1})$	39.5136	39.5102	39.5146	39.5142
$-\Delta_c U_{\text{m}}^0/(\text{kJ} \cdot \text{mol}^{-1})$	7042.6	7042.0	7042.8	7042.7
	$\langle \Delta_c u^0 \rangle = -(39.5132 \pm 0.0048) \text{ kJ} \cdot \text{g}^{-1a}$			
	$\langle \Delta_c U_{\text{m}}^0 \rangle = -(7042.5 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1a}$			

<sup>a</sup> Mean value and twice the overall standard deviation of the mean.

naphthalene and anthracene belong to space group  $\text{P2}_1/\text{a}$ .<sup>(17)</sup> The peak at  $T = 581.4$  K is possibly due to the phase transition from  $\text{P}\bar{1}$  to  $\text{P2}_1/\text{a}$ .

#### 4. Discussion

The standard molar enthalpy of combustion of phenanthrene,  $-(7048.7 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$ , agrees very well with the value of  $-(7048.05 \pm 1.46) \text{ kJ} \cdot \text{mol}^{-1}$  by Steele *et al.*,<sup>(4)</sup> who pointed out that the value selected by Pedley *et al.*,  $-(7054.5 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(18)</sup> failed to predict the equilibrium constant in the (phenanthrene + hydrogen + 9,10-dihydrophenanthrene) system.<sup>(19)</sup> The standard molar enthalpy of combustion of phenanthrene is now confirmed by the perfect agreement between two independent determinations.

TABLE 3. Summary of combustion calorimetric results for naphthacene:  $m$ , mass of naphthacene;  $m(\text{soot})$ , mass of soot; the other symbols are similar to those in table 2. Both  $\Delta_c u^0$  and  $\Delta_c U_m^0$  are derived by correction for soot formation, assuming that  $-\Delta_c u^0(\text{soot}) = 33 \text{ kJ} \cdot \text{g}^{-1}$

Expt. No.	1	2	3	4
$m/\text{mg}$	3.1642	3.2742	3.1654	3.1946
$m(\text{Vas})/\text{mg}$	0.0353	0.0420	0.0499	0.0632
$n(\text{HNO}_3)/\mu\text{mol}$	0.067	0.054	0.040	0.056
$\varepsilon^i/(\text{J} \cdot \text{K}^{-1})$	0.425	0.425	0.425	0.434
$\varepsilon^f/(\text{J} \cdot \text{K}^{-1})$	0.430	0.430	0.430	0.439
$(T_i/\text{K}) - 273.15$	23.61353	23.61334	23.61398	23.61314
$(T_f/\text{K}) - 273.15$	25.483889	25.543413	25.492010	25.514180
$\Delta T_c/\text{K}$	0.016385	0.008831	0.015054	0.013056
$\Delta T_{\text{ad}}/\text{K}$	1.85397	1.92125	1.86298	1.88798
$\Delta U_{\text{ign}}/\text{J}$	0.087	0.043	0.065	0.046
$-\Delta_{\text{IBP}}U/\text{J}$	126.448	131.084	127.084	128.827
$\Delta U(\text{HNO}_3)/\text{J}$	0.004	0.003	0.002	0.003
$\Delta U_{\Sigma}/\text{J}$	0.084	0.087	0.084	0.085
$m(\text{soot})/\text{mg}$	0.0	0.0	0.0019	0.0017
$-\Delta_c u^0/(\text{kJ} \cdot \text{g}^{-1})$	39.4186	39.4164	39.4129	39.4034
$-\Delta_c U_m^0/(\text{kJ} \cdot \text{mol}^{-1})$	8999.0	8998.5	8997.7	8995.5
	$\langle \Delta_c u^0 \rangle = -(39.4128 \pm 0.0081) \text{ kJ} \cdot \text{g}^{-1}{}^a$			
	$\langle \Delta_c U_m^0 \rangle = -(8997.7 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}{}^a$			

<sup>a</sup> Mean value and twice the overall standard deviation of the mean.

Recently, the standard molar enthalpy of combustion of anthracene was determined to be  $-(7065.0 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$  by high-precision micro-combustion calorimetry.<sup>(9)</sup> The standard molar enthalpies of formation of anthracene and phenanthrene in the crystalline state are derived to be  $(126.7 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$  and  $(110.4 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, by using the recommended values:  $\Delta_f H_m^0(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_f H_m^0(\text{H}_2\text{O}, \text{l}) = -(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$ .<sup>(11)</sup> Table 4 summarizes the derived thermodynamic quantities. The standard molar enthalpy of the rearrangement reaction  $\Delta_r H_m^0$  from anthracene to phenanthrene is attributed mainly to the difference of resonance energy. The present work shows  $\Delta_r H_m^0 = -(28.4 \pm 4.1) \text{ kJ} \cdot \text{mol}^{-1}$ , while a value of  $-(23.4 \pm 2.8) \text{ kJ} \cdot \text{mol}^{-1}$  is derived from the thermochemical data compiled by Pedley *et al.*<sup>(18)</sup>

The standard molar enthalpy of combustion of naphthacene was determined to be  $-(9005.1 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$ . The standard molar enthalpy of formation of naphthacene in the crystalline state is derived to be  $(206.9 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$ . Adopting a literature value of the molar enthalpy of sublimation  $\Delta_{\text{sub}} H_m^0 = (124.7 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(16)</sup>

TABLE 4. Derived molar thermodynamic quantities at  $T = 298.15$  K

	Phenanthrene	Anthracene	Naphthacene
$\Delta_c H_m^0(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$-7048.7 \pm 0.9$	$-7065.0 \pm 1.1$	$-9005.1 \pm 1.8$
$\Delta_f H_m^0(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$110.4 \pm 1.0$	$126.7 \pm 1.1$	$206.9 \pm 1.9$
$\Delta_{\text{sub}} H_m^0/(\text{kJ} \cdot \text{mol}^{-1})$	$91.3 \pm 2.7^{(14)}$	$103.4 \pm 2.7^{(14)}$	$124.7 \pm 4.0^{(16)}$
$\Delta_f H_m^0(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$	$201.7 \pm 2.9$	$230.1 \pm 2.9$	$331.6 \pm 4.4$

the standard molar enthalpy of formation of naphthacene in the gas phase is derived to be  $(331.6 \pm 4.4) \text{ kJ} \cdot \text{mol}^{-1}$ . The literature values of the sublimation enthalpy scatter from  $117 \text{ kJ} \cdot \text{mol}^{-1}$  to  $144 \text{ kJ} \cdot \text{mol}^{-1}$ .<sup>(20)</sup> The purity of the present sample has not been confirmed yet. Therefore, an error greater than  $4.4 \text{ kJ} \cdot \text{mol}^{-1}$  is possible.

In 1951, Magnus *et al.* reported the standard molar enthalpy of combustion of naphthacene to be  $-(8956.9 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ .<sup>(21)</sup> However, in 1969, Dewar and de Llano<sup>(6)</sup> showed, on the basis of a semi-empirical calculation, that the atomization energy had an error of  $43 \text{ kJ} \cdot \text{mol}^{-1}$ . Recently, theoretical studies<sup>(7)</sup> indicated a similar error. Naphthacene is known to be sensitive to oxygen in solution. In the present study, however, no oxidation was observed in the solid state, although Dewar and de Llano suggested that oxidation occurred in the combustion bomb before ignition.<sup>(6)</sup> Magnus *et al.*<sup>(21)</sup> reported the melting temperature of naphthacene to be (608 to 610) K, which is lower than the value of 623.2 K obtained in the present study. The sample of Magnus *et al.* was, possibly, significantly oxidized before their calorimetric measurements.

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