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# Standard molar enthalpy of formation, vapour pressures, and standard molar enthalpy of sublimation of benzanthrone

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The standard ($p^{\circ} = 0.1$ MPa) molar enthalpy of combustion at $T = 298.15$ K of crystalline benzanthrone was determined as $\Delta_{c}H^{\circ}_{m} = -(8114.7 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$ by static-bomb calorimetry, and the standard molar enthalpy of formation of the crystal at $T = 298.15$ K was derived as $\Delta_{f}H^{\circ}_{m}(\mathrm{cr}) = -(4.1 \pm 3.0)\ \mathrm{kJ \cdot mol^{-1}}$. Vapour pressure as a function of temperature was measured using the mass-loss Knudsen effusion technique, from which the standard molar enthalpy of sublimation at $T = 298.15$ K was derived as $\Delta^{g}_{cr}H^{\circ}_{m} = (126.6 \pm 0.6)\ \mathrm{kJ \cdot mol^{-1}}$. The standard molar enthalpy of sublimation at $T = 298.15$ K was also measured by the quartz oscillator method, $\Delta^{g}_{cr}H^{\circ}_{m} = (129.7 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$.
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KEYWORDS: standard molar enthalpy of combustion; standard molar enthalpy of formation; standard molar enthalpy of sublimation; vapour pressures; benzanthrone

## 1. Introduction

Benzanthrone is the trivial name of 7H-Benz[*d*, *e*]anthracen-7-one, which can be prepared by heating a reduction product of anthraquinone with sulfuric acid and glycerol(1, 2) (see figure 1).

It can be purified from ethanol, or xylene, yielding pale yellow needles with a melting point of $T_{m} = 443.15$ K, as well as by sublimation at low pressure. It is insoluble in water, but soluble in glacial acetic acid, benzene, chlorobenzene, and in sulfuric acid gives an orange solution with a green fluorescence.

The standard molar enthalpy of sublimation of benzanthrone has been previously determined by Inokuchi *et al.*,(3) Yanson *et al.*,(4) and lately by Burkinshaw and Mortimer,(5) and since then has been used as a test substance(6) for measuring enthalpies of sublimation

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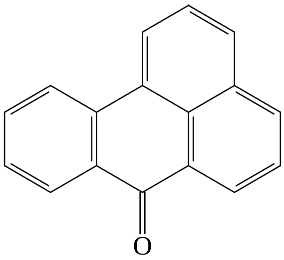

FIGURE 1. Structure of benzanthrone.

of organic solids of low volatility, by means of the differential Knudsen effusion method in conjunction with a quartz oscillator as a highly sensitive detector.

Despite its application as a test substance, the thermodynamic properties of this compound have not been well defined so far. This paper reports the measurements of the standard molar enthalpy of combustion of the crystalline solid, the vapour pressure as a function of temperature, and the standard molar enthalpy of sublimation determined by the mass-loss Knudsen effusion method and by a quartz oscillator method.

## 2. Experimental

Benzanthrone (Aldrich Chemical Co.) was purified(1) by repeated crystallization from tetrachloroethane followed by repeated sublimation at low pressure. The purification process was repeated until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The purity of the compound was checked by elemental analyses; the mass fractions $w$ of C, H, and O were: $C_{17}H_{10}O$, obtained: $10^2 \cdot w(\mathrm{C}) = 88.60$, $10^2 \cdot w(\mathrm{H}) = 4.40$, $10^2 \cdot w(\mathrm{O}) = 6.92$; expected: $10^2 \cdot w(\mathrm{C}) = 88.67$, $10^2 \cdot w(\mathrm{H}) = 4.38$, $10^2 \cdot w(\mathrm{O}) = 6.95$.

The energy of combustion of benzanthrone was measured in a static bomb calorimeter; the calorimeter, subsidiary apparatus, and technique have been described previously.(7, 8) The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard CRM-190p) having a massic energy of combustion, under standard bomb conditions, of $-(26431.8 \pm 3.7)\ \mathrm{J \cdot g^{-1}}$. The calibration results were corrected to give the energy equivalent $\varepsilon$(calor) corresponding to the average mass of water added to the calorimeter, 3119.6 g. From eight calibration experiments, $\varepsilon(\mathrm{calor}) = (16017.0 \pm 1.3)\ \mathrm{J \cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean.

The samples of benzanthrone, in pellet form, were ignited at $T = 298.15$ K in oxygen at the pressure 3.04 MPa with 1.00 $\mathrm{cm^3}$ of water added to the bomb. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16250\ \mathrm{J \cdot g^{-1}}$;(9) this value has been experimentally confirmed in our laboratory. Corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$ for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ $HNO_3(aq)$ from $N_2(g)$, $O_2(g)$, and $H_2O(l)$.$^{(10)}$

The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that from the cotton-thread fuse. The average ratios of the mass of carbon dioxide produced by benzanthrone in the combustion experiments to that calculated from the mass of sample used was $(0.9996 \pm 0.0001)$. For benzanthrone, $(\partial u/\partial p)_T$ at $T = 298.15$ K was assumed to be $-0.1\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$, a typical value for most organic solids. For each experiment, the value of $\Delta_c u^o$ was calculated by using the procedure given by Hubbard *et al.*$^{(9)}$

The vapour pressure of benzanthrone as a function of temperature were measured using a mass-loss Knudsen effusion apparatus. The detailed description of the apparatus, procedure, and technique, and results obtained with test substances (benzoic acid and ferrocene) have been reported.$^{(11)}$ This apparatus enables the simultaneous operation of three Knudsen cells, with three different holes.

In each effusion experiment, the mass loss of the crystalline samples $\Delta m$ was measured by weighing the cells with the samples within $\pm$ 0.01 mg before and after a convenient effusion time period $t$ in a system evacuated to near $p = 1 \cdot 10^{-4}$ Pa. The cells were immersed in a thermostatically controlled oil-bath. In each effusion experiment, at the temperature $T$, the vapour pressure $p$ was calculated by using the Knudsen equation:$^{(12)}$

$$p = (\Delta m/A_0 w_0 t)(2\pi RT/M)^{1/2}, \tag{1}$$

in which $M$ is the molar mass of the effusing vapour, $R$ is the gas constant, $A_0$ is the area of the effusion hole, and $w_0$ the Clausing factor $w_0 = \{1+(3l/8r)\}^{-1}$, where $l$ is the thickness of the effusion hole and $r$ is the radius. The thickness of the effusion holes $l$ was 0.049 mm, and their areas and Clausing factors were: hole 1, $A_0 = 0.596\ \mathrm{mm^2}$, $w_0 = 0.959$; hole 2, $A_0 = 0.813\ \mathrm{mm^2}$, $w_0 = 0.965$; hole 3, $A_0 = 0.862\ \mathrm{mm^2}$, $w_0 = 0.966$.

To derive the standard molar enthalpy of sublimation at the mean temperature $\langle T \rangle$ of the experimental temperature range $\Delta_{cr}^{g} H_m^o(\langle T \rangle)$, the integrated form of the Clausius–Clapeyron equation:

$$\ln(p/\mathrm{Pa}) = a - b \cdot (\mathrm{K}/T), \tag{2}$$

where $b = \Delta_{cr}^{g} H_m^o(\langle T \rangle)/R$, was used.

The standard molar enthalpy of sublimation of benzanthrone was also derived from measurements using a Knudsen effusion method with a quartz microbalance, as described by Burkinshaw and Mortimer.$^{(5)}$ The vapour effusing from the Knudsen cell was allowed to condense onto a quartz crystal positioned above the effusion hole.

The measurements were made with an Edwards 306 vacuum-coating unit, fitted with a film thickness monitor (Edwards FTM3) incorporating a quartz crystal oscillator (6 MHz), but with some modifications from the apparatus described by Burkinshaw and Mortimer.$^{(5)}$ The cylindrical Knudsen cell was made of steel (o.d. 13 mm, i.d. 6 mm, length 8 mm). The lid with an effusion-hole diameter of 0.8 mm was screwed on to the cell. The complete cell was then screwed into an electrically heated cylindrical steel block, and the temperature was controlled within $\pm$ 0.1 K by a proportional integral derivative controller, Eurotherm 815. Temperatures were measured by a Labfacility P100/0620 platinum-sensing detector screwed into the effusion cell. Frequency changes in the quartz-crystal oscillator circuit were measured with a Philips Frequency Counter PM6685 connected to the FTM3 film-thickness monitor.

The change in frequency of a quartz crystal $\Delta f$ is directly proportional(13) to the mass of the substance deposited on its surface $m$, assuming that the total frequency change is small when compared with $f$. The relation between $\Delta f$ and $m$ was derived for AT-cut quartz crystals vibrating in thickness shear mode, and can be expressed as:

$$\Delta f = (f^2/A\rho N)\cdot m, \tag{3}$$

where $f$ is the average resonance frequency, $A$ and $\rho$ are, respectively, the surface area and the density of the quartz crystal, and $N$ is the quartz crystal frequency constant, defined by $N = f\cdot l$, where $l$ is the thickness of the quartz plate (for an AT-cut quartz crystal $N = 1.67\cdot 10^3\ \mathrm{Hz\cdot m}$).

During an effusion experiment, the change in the resonance frequency $\nu = \Delta f/t$ is proportional to the rate of sublimed mass $\Delta m/t$ of the crystalline sample and to the vapour pressure:

$$\Delta m/t = pA_0w_0(M/2\pi RT)^{1/2}, \tag{4}$$

where $p$ is the vapour pressure, $A_0$ is the hole area, and $w_0$ is the Clausing factor. Then:

$$\nu = \Delta f/t = c\Delta m/t = cpA_0w_0(M/2\pi RT)^{1/2}, \tag{5}$$

or, rearranging:

$$p = \nu T^{1/2}\{(2\pi R/M)^{1/2}/(cA_0w_0)\}. \tag{6}$$

The integrated form of the Clausius–Clapeyron equation:

$$\ln(\nu T^{1/2}) = \ln B - \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}/RT, \tag{7}$$

was used to derive the standard molar enthalpy of sublimation at the mean temperature of the experimental range $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)$.

The values of the standard molar enthalpy of sublimation at the mean temperature of the experimental temperature range, obtained by both methods, were corrected to $T = 298.15$ K using the relation:

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T = 298.15\ \mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle) + \Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K} - \langle T\rangle), \tag{8}$$

where the value of the standard molar heat capacity of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}} = -50\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ was assumed in accordance with estimations made by other authors.(5) The molar masses used for the elements were those recommended by IUPAC in 1995.(14)

## 3. Results

The results of the combustion experiments are given in table 1, where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from the average mass assigned to $\varepsilon$(calor), $\Delta U_\Sigma$ is the correction to the standard state, and the remaining quantities are as described previously.(9) As samples were ignited at $T = 298.15$ K:

$$-\Delta U(\mathrm{IPB}) = \{\varepsilon(\mathrm{calor}) + \Delta m(\mathrm{H_2O})\cdot c_p(\mathrm{H_2O, l}) + \varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}}. \tag{9}$$

TABLE 1. Combustion results for benzanthrone at $T = 298.15$ K

| | | | | | | |
|---|---|---|---|---|---|---|
| $m(CO_2)/g$ | 2.43725 | 2.33787 | 2.40459 | 2.09834 | 2.35184 | 2.37106 |
| $m'(\mathrm{cpd})/g$ | 0.74857 | 0.71798 | 0.73856 | 0.64433 | 0.72242 | 0.72798 |
| $m''(\mathrm{fuse})/g$ | 0.00310 | 0.00313 | 0.00302 | 0.00297 | 0.00284 | 0.00355 |
| $\Delta T_{ad}/K$ | 1.64900 | 1.58180 | 1.62672 | 1.41950 | 1.59123 | 1.60440 |
| $\varepsilon(\mathrm{calor})/(J \cdot K^{-1})$ | 16017.4 | 10017.4 | 16017.0 | 16017.0 | 16017.0 | 16017.4 |
| $\varepsilon_f/(J \cdot K^{-1})$ | 15.72 | 15.67 | 15.71 | 15.51 | 15.67 | 15.69 |
| $\Delta m(H_2O)/g$ | 0.1 | 0.1 | 0.2 | 0.0 | 0.0 | 0.1 |
| $-\Delta U(\mathrm{IBP})/J$ | 26437.46 | 25359.95 | 29081.00 | 22756.96 | 25510.48 | 25722.68 |
| $-\Delta U(HNO_3)/J$ | 5.07 | 3.60 | 4.24 | 4.75 | 4.53 | 4.01 |
| $-\Delta U(\mathrm{ign.})/J$ | 1.19 | 1.19 | 1.09 | 1.18 | 1.19 | 0.84 |
| $\Delta U_\Sigma/J$ | 18.17 | 17.33 | 17.89 | 15.36 | 17.45 | 17.61 |
| $-m''\Delta_c u^o(\mathrm{fuse})/J$ | 50.34 | 50.83 | 49.04 | 48.23 | 46.12 | 57.65 |
| $-\Delta_c u^o(\mathrm{cpd})/(J \cdot g^{-1})$ | 35218.99 | 35221.30 | 35216.95 | 35212.73 | 35218.27 | 35225.43 |

From the combustion results listed in table 1, the mean value of the massic energy of combustion and its standard deviation are $\langle \Delta_c u^o \rangle = -(35219.0 \pm 1.7)\ J \cdot g^{-1}$. For the molar quantities at $T = 298.15$ K: $\Delta_c U_m^o = -(8109.7 \pm 2.0)\ kJ \cdot mol^{-1}$ and $\Delta_c H_m^o = -(8114.7 \pm 2.0)\ kJ \cdot mol^{-1}$. With $\Delta_f H_m^o(H_2O, l) = -(285.830 \pm 0.040)\ kJ \cdot mol^{-1}$,(15) and $\Delta_f H_m^o(CO_2, g) = -(393.51 \pm 0.13)\ kJ \cdot mol^{-1}$,(15) then $\Delta_f H_m^o(C_{17}H_{10}O, cr) = -(4.1 \pm 3.0)\ kJ \cdot mol^{-1}$. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpy of combustion and formation are twice the standard deviation of the mean, and include the uncertainties in calibration and in the values of the auxiliary quantities used.

The experimental results obtained from each cell, at different temperatures for the equilibrium vapour pressures, together with the residuals of the Clausius–Clapeyron equation for benzanthrone are presented in table 2. These results and the global ones obtained with the three cells used are fitted with equation (2) by using a least-squares computer program. The plot of $\ln p = f(1/T)$ for the individual effusion holes used for benzanthrone is presented in figure 2.

The detailed parameters of the Clausius–Clapeyron equation, the mean temperature of the experiments $\langle T \rangle$, the standard molar enthalpy of sublimation at $T = 298.15$ K $\Delta_{cr}^g H_m^o(T = 298.15\ K)$, and the value for the global treatment of all $(p, T)$ points obtained are listed in table 3. The calculated enthalpies of sublimation obtained for each individual hole are in agreement within experimental error. The mean of these values is also similar to the value derived from the overall treatment of the global results.

Table 4 lists the $(p, T)$ values calculated over the vapour pressure range $p = 0.1$ Pa to $p = 1.0$ Pa from the overall treatment.

In table 5, the results of the effusion experiments with the quartz-crystal microbalance for the determination of the standard molar enthalpy of sublimation of benzanthrone are summarized. The plot of $\ln(\nu T^{1/2}) = f(1/T)$ is shown in figure 3. From the slope

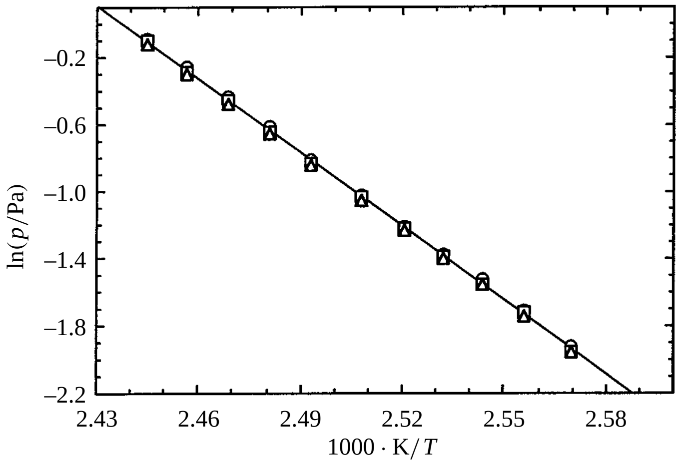

FIGURE 2. Plot of $\ln p$ against $1/T$ for benzanthrone: ○, hole 1; □, hole 2; △, hole 3.

TABLE 2. Experimental Knudsen effusion results for vapour pressure $p$, and residuals $\Delta \ln(p/\text{Pa})$ of the Clausius–Clapeyron equation for benzanthrone

| $T$/K | $p$/Pa hole 1 | $p$/Pa hole 2 | $p$/Pa hole 3 | | $10^2 \cdot \Delta \ln(p/\text{Pa})$ hole 1 | $10^2 \cdot \Delta \ln(p/\text{Pa})$ hole 2 | $10^2 \cdot \Delta \ln(p/\text{Pa})$ hole 3 |
|---|---|---|---|---|---|---|---|
| 389.20 | 0.1461 | 0.1410 | 0.1413 | | −0.81 | −2.02 | −1.13 |
| 391.26 | 0.1806 | | 0.1792 | 0.1756 | 0.59 | 2.12 | 0.88 |
| 393.15 | 0.2187 | 0.2101 | 0.2109 | | 1.75 | 0.01 | 1.29 |
| 394.94 | 0.2535 | 0.2487 | 0.2465 | | −0.36 | −0.02 | 0.08 |
| 396.75 | 0.2989 | 0.2957 | 0.2905 | | −0.79 | 0.35 | −0.34 |
| 398.72 | 0.3610 | 0.3566 | 0.3485 | | −0.14 | 0.82 | −0.29 |
| 401.12 | 0.4438 | 0.4369 | 0.4297 | | −1.45 | −0.88 | −1.22 |
| 403.10 | 0.5428 | | 0.5254 | 0.5216 | 0.76 | −0.38 | 0.31 |
| 405.10 | 0.6455 | 0.6327 | 0.6234 | | 0.16 | 0.24 | 0.28 |
| 407.11 | 0.7712 | 0.7480 | 0.7382 | | 0.12 | −0.89 | −0.59 |
| 409.04 | 0.9143 | 0.9003 | 0.8856 | | 0.17 | 0.65 | 0.72 |

of the straight line obtained, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(T = 381.9\ \text{K}) = (125.5 \pm 2.1)\ \text{kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(T = 298.15\ \text{K}) = (129.7 \pm 2.1)\ \text{kJ} \cdot \text{mol}^{-1}$.

TABLE 3. Knudsen effusion results for benzanthrone, where $a$ and $b$ are from the Clausius–Clapeyron equation, $\ln(p/\mathrm{Pa}) = a - b \cdot (\mathrm{K}/T)$, and $b = \Delta_{cr}^{g} H_m^o(\langle T \rangle)/R$; $R = 8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$

| Hole number | $a$ | $b$ | $\langle T \rangle/\mathrm{K}$ | $\Delta_{cr}^{g} H_m^o(\langle T \rangle)$ / $\mathrm{kJ \cdot mol^{-1}}$ | $\Delta_{cr}^{g} H_m^o(T = 298.15\ \mathrm{K})$ / $\mathrm{kJ \cdot mol^{-1}}$ |
|---|---|---|---|---|---|
| 1 | 35.69 ± 0.18 | 14636 ± 70 | | | |
| 2 | 35.73 ± 0.22 | 14662 ± 86 | | | |
| 3 | 35.51 ± 0.16 | 14579 ± 65 | | | |
| Global results | 35.65 ± 0.19 | 14626 ± 75 | 399.15 | 121.6 ± 0.6 | 126.6 ± 0.6 |

TABLE 4. The pressure $p$ and temperature $T$ values from the vapour pressure equation for benzanthrone

| $p/\mathrm{Pa}$ | $T/\mathrm{K}$ | $p/\mathrm{Pa}$ | $T/\mathrm{K}$ |
|---|---|---|---|
| 0.1 | 385.38 | 0.6 | 404.47 |
| 0.2 | 392.54 | 0.7 | 406.20 |
| 0.3 | 396.86 | 0.8 | 407.71 |
| 0.4 | 399.99 | 0.9 | 409.06 |
| 0.5 | 402.44 | 1.0 | 410.27 |

TABLE 5. Experimental values of the change of frequency of the quartz oscillator $\nu$ at different temperatures $T$ by deposition of benzanthrone

| $T/\mathrm{K}$ | $\nu/\mathrm{s}^{-2}$ | $T/\mathrm{K}$ | $\nu/\mathrm{s}^{-2}$ |
|---|---|---|---|
| 372.8 | 0.11632 | 383.0 | 0.32972 |
| 373.7 | 0.12337 | 384.3 | 0.38199 |
| 374.7 | 0.13619 | 387.0 | 0.49429 |
| 375.3 | 0.15093 | 388.7 | 0.57582 |
| 376.1 | 0.16917 | 390.9 | 0.75315 |
| 377.6 | 0.19021 | 392.0 | 0.78205 |
| 379.0 | 0.22051 | 393.5 | 0.94176 |
| 380.5 | 0.25927 | | |

## 4. Discussion

For benzanthrone there are three previously reported values for the standard molar enthalpy of sublimation: the value of 115.5 $\mathrm{kJ \cdot mol^{-1}}$ at $T = 398$ K, determined by Inokuchi *et al.*(3) using the mass-loss Knudsen effusion technique, yields the value of 120.5 $\mathrm{kJ \cdot mol^{-1}}$ at

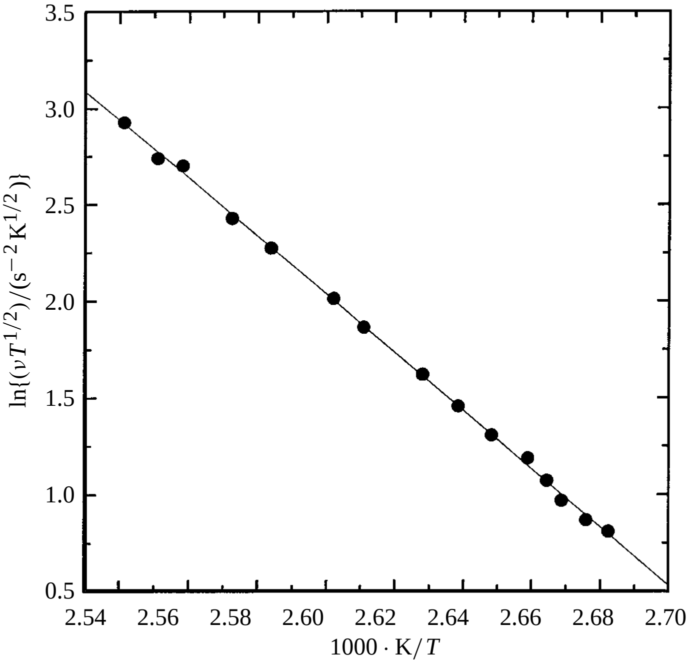

FIGURE 3. Plot of $\ln(\nu T^{1/2})$ against $1/T$ for benzanthrone.

$T = 298.15$ K; the value of (114.2±0.8) kJ · mol$^{-1}$, determined by Yanson *et al.*(4) using the quartz oscillator method, although the temperature to which it refers is not given; the value of (119.7 ± 5.4) kJ · mol$^{-1}$ at $T = 370$ K, determined by Burkinshaw and Mortimer(5) using the quartz oscillator method, which yields the value of (125 ± 6) kJ · mol$^{-1}$ for $T = 298.15$ K.

The values obtained in this work by two different experimental techniques are in mutual agreement taking into consideration the uncertainties ascribed to them, and also agree with the value determined by Burkinshaw and Mortimer(5) using the quartz oscillator detector. The Knudsen mass-loss effusion technique is a more accurate method, taking into account that the experimental effusion conditions are closer to the theoretical ones which are the basis of the Knudsen theory: this method allows the calculation of vapour pressures of the crystalline solid at different temperatures, whereas the quartz oscillator method only yields a quantity which is proportional to the vapour pressure.

Although the quartz oscillator method allows, with sufficient accuracy for most of the necessities, the determination of standard molar enthalpies of sublimation for low vapour pressure solids, and has the practical experimental advantages of requiring a much smaller amount of sample, a less sophisticated experimental device, and of being a faster and easier experimental method, it is not the preferred experimental method.

Taking into account all the above experimental limitations, the value of the standard molar enthalpy of sublimation derived from the Knudsen mass-loss effusion technique is preferred as a more accurate value for this property.

There are no previously determined values for the standard molar enthalpy of formation of benzanthrone in the literature, and an insufficient number of thermochemical results for compounds containing similar structures are available to permit estimation of an expected value for this enthalpy of formation.

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## REFERENCES

1. Macleod, L. C.; Allen, C. F. H. *Org. Syntheses* **1943**, 2, 62–64.
2. U.S.Pat. **1927**, 1, 626, 392.
3. Inokuchi, H.; Sukekuni, S.; Handa, T. *Bull. Chem. Soc. Jpn.* **1952**, 25, 299–302.
4. Yanson, I. K.; Teplitsky, A. B.; Sukhodub, L. F. *Biopolymers* **1979**, 18, 1149–1170.
5. Burkinshaw, P. M.; Mortimer, C. T. *J. Chem. Soc. Dalton* **1984**, 75–77.
6. Mortimer C.T. University of Keele, U.K. Personal communication. **1987**.
7. Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *J. Chem. Thermodynamics* **1984**, 16, 1149–1155.
8. Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *Rev. Port. Quim.* **1984**, 26, 163–172.
9. Hubbard, W.N.; Scott, D.W.; Waddington, G. *Experimental Thermochemistry*, Vol.1. Rossini, F.D.: editor. Interscience: New York. **1956**, Chap. 5.
10. The NBS Tables of Chemical Thermodynamics Properties. *J. Phys. Chem. Ref. Data* **1982**, 11, Suppl. No. 2.
11. Ribeiro da Silva, M. A. V.; Monte, M. J. S. *Thermochim. Acta* **1990**, 171, 169–183.
12. Whitman, C. I. *J. Chem. Phys.* **1952**, 20, 161–164.
13. Sauerbrey, G. *Z. Phys.* **1959**, 155, 206–222.
14. Coplen, T. B. *J. Phys. Chem. Ref. Data* **1997**, 26, 1239–1253.
15. Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *Codata Key Values for Thermodynamics*. Hemisphere: New York. **1989**.

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