Heats of Sublimation of Condensed Polynuclear Aromatic Hydrocarbons

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Introduction

Wolf and Weghofer⁽¹⁾ have found that there is an additivity in molar heats of sublimation among benzene, naphthalene and anthracene. In the previous investigation,⁽²⁾ one of the present authors (H. I.) also has found the similar additivity among the condensed polynuclear aromatic compounds of the higher molecular weights. In this previous work, however, the experimental method used was not a legitimate one and the number of compounds investigated was also restricted. In the present investigation, the orthodox molecular effusion method following Knudsen⁽³⁾ for measurement of vapour pressure was applied to the extended number of hydrocarbons.

Materials

Anthracene was purified from commercial product through anthraquinone and anthrone. Recrystallized from toluene and ethyl alcohol solution. This product, denoted as anthracene I, is white crystal with deep violet coloured fluorescence. Anthracene I was sublimed in vacuum, and obtained a product made of white crystals showing feeble fluorescence. This is denoted as anthracene II (m. p. 219°C.).

Phenanthrene was purified from commercial product by chromatography, recrystallized from ethyl alcohol solution. The product with blue coloured fluorescence was sublimed in vacuum.

Pyrene was synthesized from biphenyl-2, 2′-diacetaldehyde following Weitzenböck,⁽⁴⁾ recrystallized from ethyl alcohol solution, and repeatedly sublimed in vacuum. The product shows slightly green coloured fluorescence (m. p. 151°C.).

Naphthacene was synthesized from α-naphthol and phthalic anhydride following Deichler and Weizmann,⁽⁵⁾ recrystallized from glacial acetic acid solution and benzene solution, then repeatedly sublimed in vacuum (m. p. 340°C.).

Perylene was synthesized from naphthalene following Scholl,⁽⁶⁾ recrystallized from benzene solution and glacial acetic acid solution, then repeatedly sublimed in vacuum. Yellow crystals with green coloured fluorescence (m. p. 261°C.).

Anthanthrene was obtained by reducing anthanthrone with zinc powder in fused mixture of sodium chloride and zinc chloride, recrystallized from benzene solution, and repeatedly sublimed in vacuum. Brownish yellow coloured (m. p. 257.5 ~258°C.).

Meso-naphthodianthrene was obtained by reducing meso-naphthodianthrone which was synthesized from anthrone, recrystallized from benzene solution, and repeatedly sublimed in vacuum. Deep green coloured.

Pyranthrene was obtained by reducing commercial pyranthrone, recrystallized from nitrobenzene solution and sublimed in vacuum.

Ovalene was synthesized from meso-naphthodianthrene following Clar,⁽⁷⁾ repeatedly sublimed in vacuum. Reddish orange coloured.

Violanthrene was obtained by reducing commercial violanthrone, repeatedly sublimed in vacuum. Deep red coloured.

All these materials are the same samples as used for the electrical conductivity measurements⁽⁸⁾ as well as the magnetic susceptibility measurements carried on in our laboratory.

Experimental Procedure

The apparatus for measuring vapour pressure by the molecular effusion method is illustrated in Fig. 1. A small vessel, sample container, made of pyrex glass is hanging from a quartz spring balance in an evacuated glass tube. The cap of the sample container is made of thin-wall pyrex glass. There is a small hole in the cap through which vapours flow to the evacuated outside by the molecular effusion.

The vapour pressure p can be determined by the well known following relation

$$p=(W/st)(2\pi RT/M)^{1/2} \qquad (1),$$

where M is the molecular weight, T is the absolute temperature, R is the gas constant, s is the

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(1) K. L. Wolf and H. Weghofer, *Z. physik. Chem.*, B **39**, 194 (1938).

(2) H. Inokuchi, *J. Chem. Soc. Japan*, **72**, 552 (1951).

(3) M. Knudsen, *Ann. d. Physik*, **28**, 999 (1909); M. Volmer, *Z. physik. Chem.*, *Bodenstein-Festband*, 863 (1931).

(4) R. Weitzenböck, *Monat. f. Chem.*, **34**, 193 (1913).

(5) C. Deichler and C. Weizmann, *Ber.*, **36**, 547 (1903).

(6) R. Scholl, *Ber.*, **43**, 2202 (1910).

(7) E. Clar and H. Frömmel, *Ber.*, **82**, 46 (1949).

(8) H. Inokuchi, This Bulletin, **24**, 222 (1951).

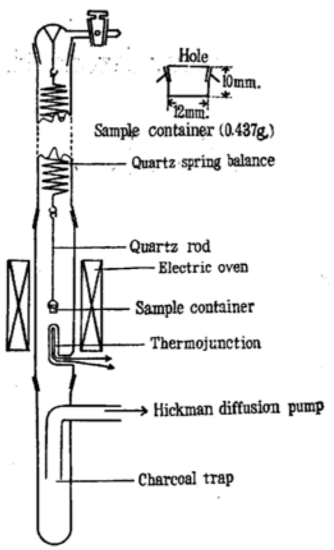

Fig. 1.—The apparatus for measuring the vapour pressure by effusion method.

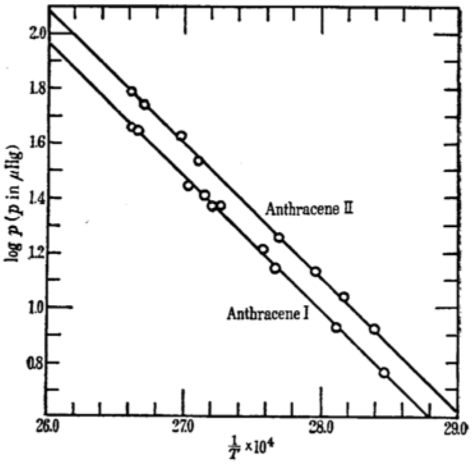

Fig. 2.—The logarithm of vapour pressure plotted against to the reciprocal temperature for anthracene.

area of the hole, and W is the mass which escapes by the effusion in time t. The cross sectional area of the hole, s, was determined by the microscope. Two kinds of hole were used, one is 0.0956 mm.^{2} and the other 0.2276 mm.^{2} in area.

The time t was measured for a constant decrease in mass, W, of the sample. The sensitivity of the spring balance was that one mg. in weight change corresponds to 0.433 mm. in elongation change, and the latter can be determined to 0.001 mm. by a microcomparator which was used as cathetometer. The temperature was controlled by supplying a stationary current to the electric oven; the constancy could be maintained within ± 0.5°C. for each temperature.

Results

A good linear relationship was found between the logarithm of vapour pressure and the reciprocal of temperature for each compound. This is illustrated in Fig. 2 for anthracene.

From the empirical equation of

$$\log p = A - B/T \qquad (2)$$

the heats of sublimation as well as the entropies of sublimation under one atmosphere are calculated by Clausius-Clapeyron's relation; $\Delta H = 2.303 \cdot R \cdot B$ and $\Delta S^\circ = 2.303 \cdot R \cdot (A - 2.8808)$.

The molar heat of sublimation (ΔH) was estimated as 22.0 kcal. for anthracene I and 22.1 kcal. for anthracene II. From these values, the inner heats of sublimation ($\Delta U = \Delta H - RT$) were determined as 21.3 kcal. and 21.4 kcal. respectively. The heat of sublimation of anthracene has been obtained by several investigators; 20.0 kcal. by Mortimer and Murphy,(9) 22.3 kcal. by Wolf and Weghofer,(1) 22.8 kcal. by Nitta, Seki and Momotani(10) and 22.3 kcal. by Magnus, Hartmann and Becker.(11) Of these values, Mortimer's result seems too small, and the others are in good agreement with our result.

The experimental results are summarized in Table 1.

In the second column of Table 1 the number of carbon atoms in each molecule are shown, and in the last column the values of inner heat of sublimation being assigned to one carbon atom are shown. It must be emphasized that the last values are nearly constant to each other. This is well illustrated in Fig. 3, where the inner heats of sublimation are plotted against the number of carbon atoms in each molecule. From the linearity of Fig. 3, the value of inner heat of sublimation assigned to one carbon atom is estimated as 1.51 kcal./mole. This is nothing but showing that there is an additivity in the heats of sublimation among the present series of compounds.(12)

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(9) F. S. Mortimer and R. V. Murphy, *Ind. Eng. Chem.*, **15**, 1140 (1923).

(10) I. Nitta, S. Seki and M. Momotani, *J. Chem. Soc. Japan*, **71**, 430 (1950).

(11) A. Magnus, H. Hartmann and F. Becker, *Z. physik. Chem.*, **197**, 75 (1951).

(12) Recently, Magnus et al.(11) have derived the heats of sublimation of some similar compounds from the integral heats of solution in xylene. In their results, five kinds of isomers of $C_{18}H_{12}$ are included. The heats of sublimation of these compounds have been found to vary from 25.4 kcal. of 3,4-benzophenanthrene to 29.7 kcal. of naphthacene. This last value is slightly larger than our result. Neverthless, the average value of five compounds is 27.1 kcal. and the assigned value to one carbon atom is about 1.51 kcal./mole.

Table 1

Heats of Sublimation of Condensed Polynuclear Aromatic Hydrocarbons

Substance	Number of C-atoms (n)	Mean exp. temperature (C°.)	$\log p = A - B/T$ (p in mm. Hg) A	$B \cdot 10^{-3}$	Inner heat of sublimation (ΔU in kcal.)	Entropy of sublimation ($\Delta S°$ in cal./deg.)	$\Delta U/n$ kcal.
Benzene*	6				9.2		1.53
Naphthalene*	10				15.3		1.53
Anthracene I	14	92	11.420	4.79_5	21.3 ± 0.5	39.1	1.52
Anthracene II	14	91	11.611	4.82	21.4 ± 0.3	40.0	1.53
Phenanthrene	14	42	12.780	4.74	21.1 ± 0.3	45.3	1.51
Pyrene	16	79	12.903	5.23	23.3 ± 0.4	45.9	1.46
Naphthacene	18	186	11.485	6.13	27.1 ± 0.7	39.4	1.51
Perylene	20	142	14.350	6.77	30.2 ± 0.5	52.5	1.51
Anthanthrene	22	206	12.889	7.06	31.3 ± 1.2	45.8	1.42
Coronene**	24	134			35.5		1.48
Meso-naphthodianthrene	28	332	13.789	9.43	42.0 ± 1.2	49.9	1.50
Pyranthrene	30	322	14.825	10.15	45.3 ± 1.6	54.7	1.51
Ovalene	32	327	15.757	11.04	49.4 ± 1.9	58.9	1.54
Violanthrene	34	317	17.532	11.68	52.3 ± 2.1	67.0	1.54

* Wolf and Weghofer's data⁽¹⁾ ** Previous work's data⁽²⁾

Table 2

Heats of Sublimation of Anthraquinone, Benzanthrone and Anthanthrone

Substance	Number of C-atoms (n_c)	Number of O-atoms (n_o)	Mean exp. temperature (C.°)	$\log p = A - B/T$ (p in mm. Hg) A	$B \times 10^{-3}$	Inner heat of sublimation (ΔU in kcal.)	Entropy of sublimation ($\Delta S°$ in cal./deg.)	$\Delta U/(n_c+n_o)$ (kcal.)
Anthraquinone	14	2	103	12.457	5.47_5	24.2 ± 0.5	43.8	1.51
Benzanthrone	17	1	125	13.432	6.03	26.8 ± 0.5	48.3	1.49
Anthanthrone	22	2	219	13.684	7.95	35.4 ± 1.2	49.4	1.48

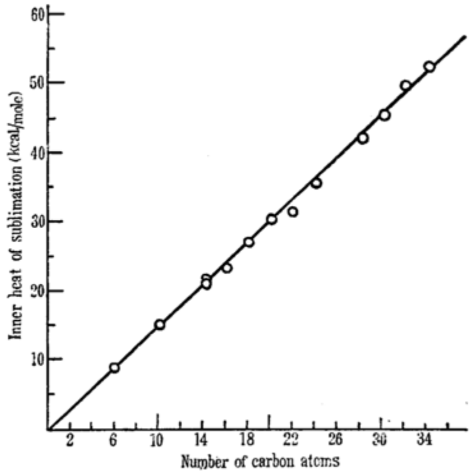

Fig. 3.—Inner heats of sublimation in kcal./mole plotted against number of carbon atoms in a molecule.

It is not unnatural to find such an additivity law, since the crystals of these compounds are made of typical molecular lattice, and the intermolecular forces will be purely based on the dispersion effect.

In the case of compounds with quinonoid structure instead of hydrocarbons, it was found that some polymerization occurs in a part of specimen during the course of sublimation at higher temperature, and the polymerization product covers the surface of specimen. This made the accurate measurement of vapour pressure difficult and the number of reliable results was restricted. In Table 2 the results are shown for anthraquinone, benzanthrone and anthanthrone. In this case too a rough additivity law seems to be found. The contribution of oxygen atom to the heat of sublimation is nearly the same as that of carbon atom.

Recently much attention has been directed to the condensed polynuclear aromatic compounds, for their interesting physical properties due to the π-electron orbitals as well as the components of coal tar. Compounds with higher molecular weights have been synthesized too. Nevertheless, as the molecular weight increases, no good solvent can be found for these compounds. In consequence, the technique of separation or purification is mostly restricted to the sublimation method, instead of the usual method through dissolution process. The additivity law in heats of sublimation will be useful for the separation and identification of these compounds in relation to each other.

Summary

The heats of sublimation of a series of condensed polynuclear aromatic hydrocarbons, from anthracene (C_{14}) to violanthrene (C_{34}), were measured. It has been found that there is an additivity in the inner heats of sublimation among these compounds, i. e., as the number of carbon atoms in each molecule increases by one, the inner heat of sublimation increases by 1.51 kcal./mole.

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