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THERMODYNAMIC STUDY OF ANTHRONE, COUMARIN AND PHENAZINE

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Anthrone, coumarin and phenazine were studied by combustion calorimetry of small amounts of substance, sublimation calorimetry, neat capacity measurements and differential thermal analysis.

The thermodynamic quantities derived at 298.15 K allowed us to determine some energy values related to molecular structure which enabled us to realize a comparative study for the two isomers: chromone and coumarin, and determine an enthalpy value for some intramolecular chemical bonds in the molecules studied.

Keywords: anthrone, combustion calorimetry, coumarin, phenazine, sublimation calorimetry

Introduction

– The title compounds are observed in pyrolysis coal products.
– Coumarin is an isomer of chromone. Both are present in plants and have many applications in medecine and perfume industry.
– Thermodynamic data on these compounds are scarce and often uncertain.
– A thermodynamic study should give further informations on the
  * intramolecular bond energies,
  * stability and specific interactions of these compounds.

Experimental

Substances:

Anthrone, coumarin (Merck) and phenazine (Aldrich) were further purified by recrystallization from ethanol and sublimation under vacuum (10^{-2} Torr) at 40°C for coumarin, 110°C for anthrone and 120°C for phenazine. The purity of

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coumarin and phenazine samples was determined by DTA (Table 1). Anthrone slightly decomposes at its melting point.

Table 1 DTA results for anthrone, coumarin and phenazine

Substance formula	purity/	T^*_{tp}/	$\Delta_{fus}H_m$/
	mol %	K	kJ·mol^{-1}
anthrone	99.8 (*)	429 (**)	26.8 (**)
coumarin	99.91±0.01	342.14±0.01 (1)	19.14±0.11
phenazine	99.99±0.01	447.89±0.01 (2)	18.88±0.14 (3)

Literature values:

(1) 341.7 K [11];

(2) 447–450 K [12]; 449–450 K [13]; 444 K [9];

(3) (20.92±0.71) kJ mol^{-1} [9]

(*) related to IPTS-68

(**) anthrone presents a slightly decomposition at its melting point. The values given in this table are purely indicative.

Combustion calorimetry

The enthalpies of combustion at 298.15 K were determined

– on 5 mg samples,

– with a CRMT rocking-calorimeter equipped with a stainless steel microbomb (Fig. 1) [1]. Experimental conditions: $V_{(bomb)}$= 42.9 cm^3, $V_{(H_2O)}$= 1 cm^3, $P_{(O_2)}$= 30.4 bar, calibration with benzoic acid NBS standard sample 39i (sensitivity=62.4 μV mW^{-1}).

Sublimation calorimetry

The enthalpies of sublimation were measured

– at 298.15 K with coumarin, at 354.4 K with anthrone and phenazine,

– on 10–30 mg samples,

– with a Tian-Calvet calorimeter equipped with a Knudsen effusion cell (Fig. 2) [2]. The effusion orifice was chosen in dependence on the vapour pressure of the substances. The calorimeter was calibrated electrically (sensitivity: 64 μVmW^{-1}).

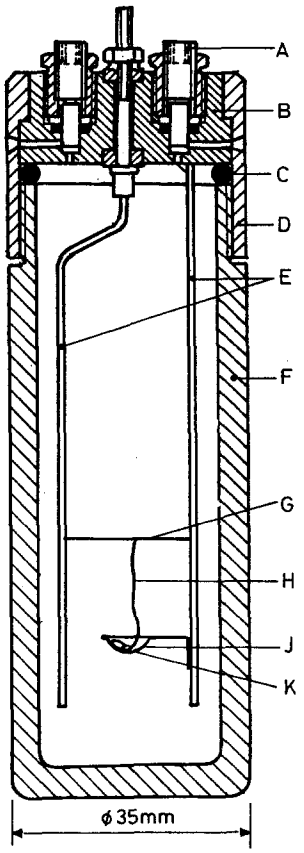

Fig. 1 Bomb for combustion of small quantities of substances;
A: gas in- or outlet, B: lid, C: toric viton joint, D: hold-down nut, E: electrodes, F: bomb body, G: Pt thread, Ø=0.05 mm, H: cotton thread, J: crucible, K: substance

Differential thermal analysis

This technique enabled us to determine the triple point temperature and the enthalpy of fusion of coumarin and phenazine (Table 1) using the apparatus and the operation mode described in Ref. [3].

Results

– The thermodynamic properties of anthrone, coumarin and phenazine are given in Table 2.

– Under Knudsen effusion conditions

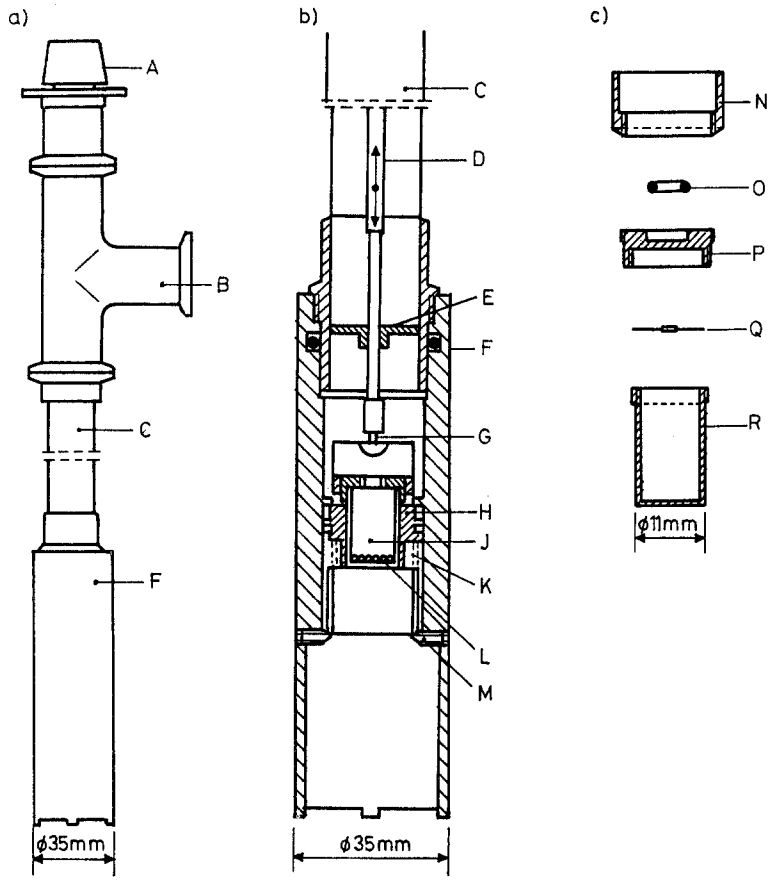

Fig. 2 Experimental apparatus for the calorimetric measurement of the enthalpy of sublimation or vaporization of a substance.
(*a*) external general view, (*b*) lower part, (*c*) effusion cell, A: opening button for obturator shaft, B: aluminumT-tube, C: stainless steel tube, D: obturator shaft, E: shaft guide, F: AU4G cylinder, G: obturator, H: AU4G tube, J: effusion cell, K: calibration resistance, L: substance, M: fixation screw of the tube H, N: upper part of the lid, O: toric viton joint, P: lower part of the lid, Q: teflon joint, R: cell body

$$P \approx \Delta P = \frac{\mathrm{d}m}{aF\mathrm{d}t}\left(\frac{2\pi RT}{M}\right)^{1/2}$$

ΔP is the difference of pressure between inside and outside the effusion cell, nearly equal to the saturated vapour pressure P of the substance, dm/dt: effusion rate, a: orifice area, F: Clausing factor, R: gaz constant, T: absolute temperature, M: molar mass.

The saturated vapour pressure is

– for coumarin at 298.15 K: 5 10^{-4} Torr,

Table 2 Thermodynamic properties of anthrone, coumarin and phenazine at 298.15 K

Substance	$\Delta_c H^\circ_m$ (s, 298.15K) / kJ·mol^{-1}	$\Delta_f H^\circ_m$ (s, 298.15K) / kJ·mol^{-1}	$\Delta_{sub} H^\circ_m$ (298.15K) / kJ·mol^{-1}	$\Delta_f H^\circ_m$ (g, 298.15K) / kJ·mol^{-1}	$\Delta_{a,exp} H^\circ_m$ (298.15K) / kJ·mol^{-1}
anthrone	−6858.4± 1.9	−79.9± 2.1	103.73± 0.63	23.4± 2.2	12439.1± 3.8
coumarin	−4139.2± 1.7	−259.9± 1.8	83.09± 0.22 (1)	−176.8± 1.8	8433.2± 2.7
phenazine	−6106.7± 3.3 (2)	241.3± 3.4	96.97± 0.36 (3)	338.3± 3.4	10951.1± 4.3

Literature values:

(1) 86.2 kJ·mol^{-1} [14];

(2) (−6109.1± 1.7 kJ·mol^{-1} [15]; (−6110.2± 6.0) kJ·mol^{-1} [9];

(3) (99.9± 2.5 kJ·mol^{-1} [15].

- for anthrone at 354.4 K: $2 \cdot 10^{-3}$ Torr,
- for phenazine at 354.4 K: $8 \cdot 10^{-3}$ Torr,

Discussion

Conjugation energy

The method for calculating the experimental and theoretical conjugation energy is described in Ref. [4].

The difference 28.3 $kJ \cdot mol^{-1}$ between the experimental values of the conjugation energy of coumarin and its isomer chromone, previously studied [5], which is equal to the difference between the enthalpies of formation in the gaseous state of the two molecules, represents the enthalpy of isomerization. Coumarin possesses the highest value of conjugation energy. It is more stable than chromone. This is probably due to the position of oxygen atom in carbonyle function which is more free in coumarin molecule.

The existence of a CH_2 group in anthrone prevents a complete conjugation of this molecule. The experimental value of the conjugation energy 325.6 $kJ \cdot mol^{-1}$ is nearly equal to those of benzophenone 336.7 $kJ \cdot mol^{-1}$ [6].

For phenazine, experimental (394 $kJ \cdot mol^{-1}$) and theoretical (379 $kJ \cdot mol^{-1}$) values of conjugation energy are quite similar. This molecule must be planar.

Atomization enthalpy

From experimental values of atomization enthalpies (Table 2), it is possible to determine:

- an energy value for C–N, C=N bonds: H(C–N, C=N)=924.2 kJ mol^{-1} which is compatible with the value (902.2 $kJ \cdot mol^{-1}$) obtained from previous studies [7, 8] and the results of McEachern (886.2–919.6 $kJ \cdot mol^{-1}$) [9],
- an energy value for C_b–(CH_2) bond: H[C_b–(CH_2)]=324 $kJ \cdot mol^{-1}$ which is in agreement with the result obtained from a study of fluorene [10].

The atomic distances between the two C_b–O bonds in coumarin are slightly different: 1.361 Å and 1.346 Å. The energy value for these two chemical bonds are respectively 366.8 and 397.7 $kJ \cdot mol^{-1}$.

References

1 R. Sabbah and I. Antipine, Bull. Soc. Chim. Fr., 3 (1990) 392.
2 R. Sabbah, I. Antipine, M. Coten and L. Davy, Thermochim. Acta, 115 (1987) 153.

3 R. Sabbah and I. Antipine, J. Thermal Anal., 32 (1987) 1929.
R. Sabbah and L. El Watik, J. Thermal Anal., 36 (1990) 2299.
4 R. Sabbah, M. Gilbert and A. Julg, Thermochim. Acta, 10 (1974) 345.
5 R. Sabbah and L. El Watik, Bull. Soc. Chim. Fr, 4 (1988) 626.
6 R. Sabbah and M. Laffitte, Thermochim. Acta, 23 (1978) 196.
7 R. Sabbah, Thermochim. Acta, 35 (1980) 73.
8 R. Sabbah and M. Laffitte, Thermochim. Acta, 25 (1978) 376.
9 D. M. McEachern, O. Sandoval and J. C. Iniguez, J. Chem. Thermodyn.,7 (1975) 299.
10 R. Sabbah, bull. Soc. Chim. Fr., 128 (1991) 350.
11 R. M. Myasnikova, T. S. Davydova and V. I. Simonov, Soc. Phys. Crystallogr., 18 (1974) 454.
12 Given by Aldrich.
13 Handbook of Chemistry and Physics, 58th Edn, R. C. Weast Ed., CRC Press, Cleveland, Ohio 1977-8.
14 V. V. Serpinskii, S. A. Voitkevich and N. Y. Lynboshits, Zh. Fiz. Khim., 27 (1953) 1032; Chem. Abstr., 49 (1955) 3594e.
15 M. R. Arshhadi, J. Chem. Thermodyn., 12 (1980) 903.

Zusammenfassung — Mittels Verbrennungskalorimetrie kleiner Substanzmengen, Sublima-tionskalorimetrie, Wärmekapazitätsmessungen und DTA wurden Anthron, Kumarin und Phenazin untersucht.
Die bei 298.15 K erhaltenen thermodynamischen Größen gestatten die Bestimmung einiger Energiewerte bezüglich der Molekülstruktur, die uns in die Lage versetzen, eine vergleichende Studie der zwei Isomere Chromon und Kumarin zu erstellen und die Enthalpiewerte für einige intramolekulare Bindungen in den untersuchten Verbindungen zu bestimmen.