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ENTHALPIES OF SUBLIMATION AND FUSION OF MONOPHENYLUREA AND DIPHENYL-1,3 UREA.

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SUMMARY

The sublimation enthalpies of monophenylurea (MPhU) and diphenyl-1,3 urea (1,3-DPhU) have been derived from the dependence of their vapour pressures on temperature, as measured by the torsion-effusion method. Values obtained are: 136 kJ mol^{-1} for MPhU and 152 kJ mol^{-1} for 1,3-DPhU, where the estimated errors are comprised within 6 kJ mol^{-1}.

Enthalpies and temperatures of fusion have been measured by differential scanning calorimetry, leading to 23.7 kJ mol^{-1} and 420.6 K for MPhU, and 34.6 kJ mol^{-1} and 512 K for 1,3-DPhU. Poor reproducibility of results for 1,3-DPhU seems be due to the beginning of decomposition. No solid-to-solid transitions have been revealed from r.t. to fusion for both compounds.

INTRODUCTION

Mono- and di-substituted derivatives of urea are often employed as "model" compounds for studies in solution (refs. 1-5), especially with respect to the influence of the substituents on the changes in water structure induced by the urea molecule (ref. 6).

The substantial lack of thermodynamic data on this class of compounds led us to look into the thermal stability and phase transitions of urea and a number of its mono- and di-substituted derivatives (refs. 7-8). It may be also noted in particular that enthalpies of sublimation (or vaporization) can be combined with enthalpies of solution at infinite dilution to obtain enthalpies of solvation, especially hydration (ref. 9). When deriving enthalpies of solvation at 298 K from enthalpies of sublimation, the enthalpic balance due to possible solid-to-solid transitions must also be taken into account (ref. 10).

This work reports vapour pressure and calorimetric measurements leading to enthalpies of sublimation and fusion, respectively, for monophenylurea (MPhU) and diphenyl-1,3 urea (1,3-DPhU).

EXPERIMENTAL PART

Materials

MPhU and 1,3-DPhU were commercial first-grade purity products (98-99%) from K&K Laboratories and Fluka, respectively. They were further purified by up to

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five successive crystallizations from ethyl acetate solutions.

Vapour pressures measurements

Vapour pressures were measured by the torsion-effusion technique (ref. 11). The method and experimental assembly employed have been described previously (ref. 12). In this study, a conventional graphite cell was used. Naphthalene and mercury were employed as reference compounds to determine the instrumental constants, as well as to assess the overall accuracy of the measurements.

Calorimetric measurements

Measurements of the enthalpies of fusion and relevant onset temperatures were made with a Setaram mod. DSC-111 G differential scanning calorimeter with output recorded on a Sefram Servotrace recorder. Areas under peaks were mesured with a Salmoiraghi mod. 237 high-precision manual planimeter. Experimental details and the procedure to convert peak areas into the associated heats by using sensitivity values are described in ref. 8. All fusion runs were performed at the heating rate of 1 K min^{-1}. For each compound, one run starting from r.t. was also performed to reveal possible solid-to-solid transitions and/or decomposition before fusion.

RESULTS AND DISCUSSION

Enthalpies of sublimation

Vapour pressure data for MPhU and 1,3-DPhU against the reciprocal absolute temperature are plotted in Fig. 1 as a result of four and six runs, respectively. Equations of the vapour pressure derived from the least squares treatment of the experimental data for each run are reported in Table 1.

By weghing slopes and intercepts according to the number of experimental data, the following equations were selected

$$\text{MPhU}, \quad \lg(p/\text{kPa}) = (15.4 \pm 0.4) - (7124 \pm 158)(\text{K}/T) \qquad (1)$$

$$\text{1,3-DPhU}, \quad \lg(p/\text{kPa}) = (14.9 \pm 0.2) - (7960 \pm 154)(\text{K}/T) \qquad (2)$$

where the associated errors are twice the weighed standard deviations. These equations are plotted in Fig. 1 (full lines) together with the straight line selected for urea (ref. 7). Comparison shows that the absolute vapour pressures of both compounds are lower than those found for urea. In particular, values for 1,3-DPhU are considerably lower than for monophenylurea. Thus the presence of two symmetric phenyl groups in the molecule seems to increase the stability of the solid phase of 1,3-DPhU by comparison with MPhU.

The sublimation enthalpies $\Delta_{sub}H° = 136$ kJ mol^{-1} at 406 K for MPhU and $\Delta_{sub}H° = 152$ kJ mol^{-1} at 464 K for 1,3-DPhU have been derived from the slopes of eqns. (1) and (2). The values are higher than those found by Kozyro and Krasulin (ref. 13) by Knudsen measurements: ca. 122 kJ mol^{-1} at 395 K for MPhU and 134 kJ mol^{-1} at 430 K for 1,3-DPhU. Critical analysis of our data, indeed, leads the conclusion that some uncertainty (systematic errors) could be ascribed to both our vapour pressure and our temperature values, but the total error for the derived sublimation enthalpies should not exceed 6 kJ mol^{-1}.

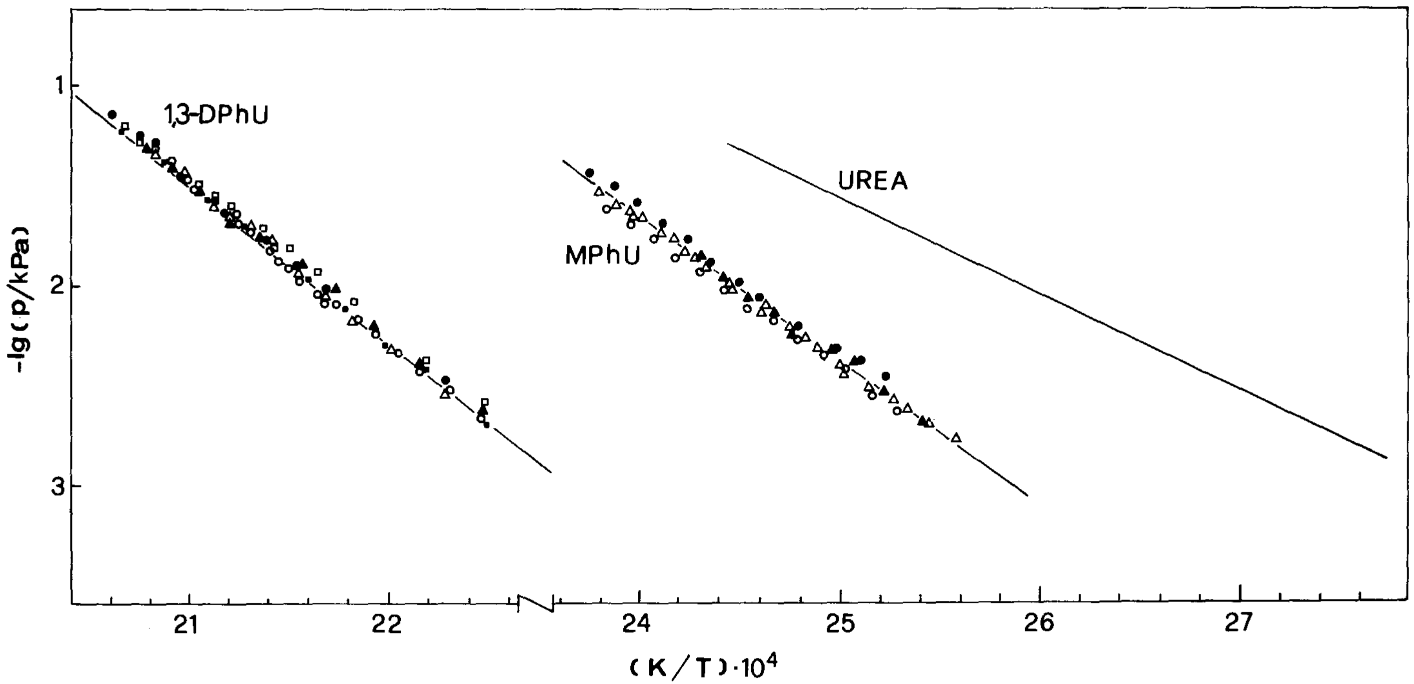

Fig. 1. Values of vapour pressure vs 1/T measured by the torsion-effusion method. MPhU: ● Run 1; ○ Run 2; △ Run 3; ▲ Run 4; 1,3-DPhU: ○ Run 1; ● Run 2; □ Run 3; △ Run 4; ▲ Run 5; ■ Run 6. The straight line of urea derived in the previous work (ref. 7) is reported for comparison.

TABLE 1

Vapor pressure against 1/T equations measured over monophenylurea and diphenyl-1,3 urea.

Compound	Run	T/K	No. of points	$\lg(p/\mathrm{kPa}) = A - B(K/T)$	
				A^a	B^a
MPhU	1	396–420	12	16.00±0.24	7344± 98
	2	396–419	13	15.06±0.10	7000± 45
	3	390–420	23	15.33±0.14	7098± 56
	4	392–412	10	15.32±0.30	7079±155
1,3-DPhU	1	445–484	20	15.16±0.35	7935±130
	2	449–483	11	14.87±0.15	7791± 70
	3	445–484	13	14.53±0.10	7611± 49
	4	449–480	11	14.35±0.15	8488± 70
	5	445–481	10	15.03±0.10	7863± 34
	6	445–484	10	15.67±0.13	8167± 63

[a] The errors are standard deviations.

TABLE 2

Measurements by DSC of temperatures and enthalpies of fusion.

Compound	m/g	T_{fus}/K	A/mm^2	$S/\ \mu V mW^{-1}$	$\Delta_{fus}H/kJ\ mol^{-1}$
MPhU	0.01819	420.7	9850	7.552	23.42
	0.01216	420.6	6600	7.552	23.49
	0.01101	420.6	6055	7.555	23.77
	0.01439	420.5	7760	7.555	23.32
	0.00793	420.8	4410	7.555	24.05
	0.00879	420.5	4880	7.555	24.02
		420.6±0.1*			23.68±0.31*
1,3-DPhU	0.00611	509.4	3370	7.929	35.44
	0.00916	513.9	4720	7.935	33.08
	0.00740	512.0	3905	7.931	33.89
	0.01169	513.0	6570	7.936	36.07
		512.1±2*			34.62±1.38*

*Mean value and standard deviation.

Enthalpies of fusion

Experimental results concerning DSC measurements for MPhU and 1,3-DPhU are reported in Table 2, where column 1 gives the amount of compound, column 2 the onset temperature of the fusion peak in K, column 3 the area, A, of the peak in mm^2, column 4 the sensitivity, S, of the heat-flux detector in μVmW^{-1} (ref. 8), and column 5 the fusion enthalpy, $\Delta_{fus}H$, in kJ mol^{-1}. The computed $\Delta_{fus}H$ and T_{fus} mean values are also reported, together with their standard deviations.

For MPhU, six calorimetric runs led to $\Delta_{fus}H = (23.68 \pm 0.31)$ kJ mol^{-1} and $T_{fus} = (420.6 \pm 0.1)$ K. The entropy of fusion derived from these data is $\Delta_{fus}S = (56.3 \pm 0.7)$ J K^{-1} mol^{-1}, in very good agreement with Walden's rule, which suggests that the enthalpy of fusion devided by melting point is equal to ca. 55 J K^{-1} mol^{-1} for non-associated substances (ref. 14).

A boiling point of around 560 K was derived from the vapour pressure of MPhU at the melting point, $p = 2.7 \times 10^{-2}$ kPa calculated by eqn. (1), by utilizing the enthalpy of fusion measured calorimetrically, and ignoring the heat content variations in the evaporation processes. This value is higher than the 511 K reported in literature (ref. 15). Enthalpy of vaporization has been estimated as around 110 kJ mol^{-1}.

In the case of 1,3-DPhu, the average temperature of fusion was (512 ± 2) K in acceptable agreement with the value of 511 K reported in literature (ref. 15). However, fusion peaks showed poor reproducibility in both their form and their associated enthalpy values, probably due to interfering thermal effects in very early stages of the decomposition process. The literature data (ref. 15) indicate a decomposition temperature of 535 K, but our experimental evidencies showed a marked baseline drift during the melting process as well as some not readily reproducible inflections after it (ca. 520 K). By selecting the best fusion peaks only among those obtained by using high-tightness stainless steel crucibles, we were able to draw an average enthalpy of fusion (34.6 ± 1.4) kJ mol^{-1}. The derived entropy of fusion was (66.5 ± 1.7) J K^{-1} mol^{-1}, noticeably higher than that expected from Walden's rule (ref. 14).

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