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Note

VAPOUR PRESSURES AND ENTHALPIES OF SUBLIMATION OF 1,3-DIMETHYL-5-ETHYLURACIL AND 1,3-DIMETHYL-5,6-PENTAMETHYLENEURACIL

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The hydration of nucleic acid bases is important for their interaction and thus for the spatial organization of the polynucleotide chains in aqueous solutions. Thus, determination of the enthalpy of interaction could be helpful in the elucidation of the nature of these interactions. The enthalpy of sublimation, ΔH_{sub}, is directly related to the enthalpy of hydration, ΔH_{hydr}, such that

$$\Delta H_{\mathrm{hydr}} = \Delta H_{\mathrm{sol}} - \Delta H_{\mathrm{sub}} \tag{1}$$

Therefore, the enthalpy of interaction can be evaluated. ΔH_{sol} is the enthalpy of solution of a given substance in water to produce an infinitely dilute solution. Knowledge of an accurate value for the enthalpy of sublimation is important because it is a significant part of the value of the enthalpy of interaction.

Teplitsky et al. [1] have determined the enthalpies of sublimation for a series of alkylated 1,3-dimethyluracil derivatives by the quartz-resonator method and field mass spectrometry using the Knudsen cell as an evaporator. The enthalpy of sublimation of 1,3-dimethyl-5-ethyluracil ($\mathrm{m}^{1,3}_{2}\mathrm{e}^{5}\mathrm{Ura}$) ($\Delta H_{\mathrm{sub}} = 110.0 \pm 1.2$ kJ mole^{-1}) was measured by the quartz-resonator method over a temperature range of 319–340 K. Both the quartz-resonator method and field mass spectrometry were employed for 1,3-dimethyl-5,6-pentamethyleneuracil [$\mathrm{m}^{1,3}_{2}(\mathrm{CH}_2)^{5,6}_{5}\mathrm{Ura}$] to yield ΔH_{sub} values of 108.8 ± 5.0 and 113.4 ± 1.3 kJ mole^{-1} over the temperature ranges 323–338 K and 340–370 K, respectively. Divergence of these results makes it necessary to determine the enthalpy of sublimation of these compounds. The chosen method (Knudsen effusion method) also enabled us to obtain accurate data for the vapour pressures of the compounds studied.

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EXPERIMENTAL

Materials

$m_2^{1,3}e^5$Ura and $m_2^{1,3}(CH_2)_5^{5,6}$Ura were prepared by synthesis procedures as described previously [1]. The melting point and degree of purity were determined using a Perkin-Elmer model 2 differential scanning calorimeter. They were 353.1 K (99.74 mass %) and 397.3 K (99.76 mass %), respectively. It is emphasized that these pure specimens were taken from exactly the same pure stock materials that had been used for the investigations carried out by Teplitsky et al. [1].

Apparatus and procedure

The saturated vapour pressure was measured by the Knudsen effusion method and a set-up identical with that described elsewhere [2]. The set-up included a stainless-steel sublimation chamber placed in an ultrathermostat and connected to a high-vacuum line (10^{-4} Pa). The substance investigated was placed in a cylindrical Knudsen cell made of duralumin and covered with a gas-tight screw-on lid. The lid was equipped with a tantalum foil (0.002 cm thick) in which an effusion orifice of a diameter 0.0923 cm and area 6.691×10^{-3} cm^2 was made. The Knudsen cell was placed at the bottom of the sublimation chamber with some Apiezon L grease applied in between to ensure a good thermal contact. The temperature inside the ultrathermostat was maintained constant to within 0.005 K and measured with the aid of a calibrated platinum resistance thermometer.

The vapour pressure, p, was evaluated from values of Δm, the mass of the substance that sublimed away in time t, and T, the temperature, by using the relationship

$$p = \frac{\Delta m}{W_a a t}\left(\frac{2\pi RT}{M}\right)^{0.5} \qquad (2)$$

where $W_a (= 0.986 \pm 0.003)$ is the Clausing coefficient of the Knudsen-cell orifice, a is the surface area of the effusion orifice, M is the molecular mass, and R is the universal gas constant.

The vapour pressure data thus obtained were correlated by a least-squares fit to the integrated form of the Clausius–Clapeyron equation, i.e.

$$\log_{10} p = -\frac{B}{T} + A \qquad (3)$$

From the slope B, the enthalpy of sublimation, at the mean value of the experimental temperature range, was calculated.

RESULTS AND DISCUSSION

The vapour pressure data obtained for $m_2^{1,3}e^5$Ura and $m_2^{1,3}(CH_2)_5^{5,6}$Ura are presented in Table 1.

The enthalpies of sublimation evaluated from eqn. (3) for the two substances are: $m_2^{1,3}e^5$Ura, $\Delta H_{sub} = 99.27 \pm 0.20$ kJ mole^{-1} at 299.63–316.45 K; $m_2^{1,3}(CH_2)_5^{5,6}$Ura, $\Delta H_{sub} = 111.88 \pm 0.20$ kJ mole^{-1} at 335.07–357.77 K.

As far as the authors are aware, the present vapour pressure data are the first to be published for the two compounds examined. As regards the enthalpy of sublimation, the present values have much smaller uncertainties (0.20 and 0.20 kJ mole^{-1}) than the only data reported so far [1] [1.2 and 1.3 kJ mole^{-1}, respectively, and even 5 kJ mole^{-1} for $m_2^{1,3}(CH_2)_5^{5,6}$Ura as measured by mass spectrometry]. The values of the enthalpy of sublimation of $m_2^{1,3}(CH_2)_5^{5,6}$Ura given by Teplitsky et al. [1] seem to be doubtful, because the values at lower temperatures (mass spectrometry) are smaller than the values obtained for higher temperatures (quartz resonator), whereas it is known that the enthalpy of sublimation is a decreasing function of temperature. Our results were obtained by a method, which was checked using compounds such as benzophenone [2], naphthalene and benzoic acid [3] when correct results were always obtained.

TABLE 1

Experimental vapour pressure data

T (K)	t (s)	Δm (mg)	p (Pa)	$\frac{10^2\delta p}{p}$
$m_2^{1,3}e^5$Ura				
299.63	24600	1.65	0.0310	−0.08
302.98	23400	2.45	0.0485	+0.37
306.57	22800	3.73	0.0764	−0.08
309.91	18660	4.61	0.116	−0.29
313.49	22500	8.59	0.180	−0.34
316.45	18600	10.16	0.259	+0.42
$m_2^{1,3}(CH_2)_5^{5,6}$Ura				
335.07	21780	1.46	0.0294	−0.18
341.63	22680	3.27	0.0639	+0.34
344.55	18900	3.77	0.0888	−0.14
347.94	21600	6.29	0.130	−0.08
354.83	19800	12.13	0.277	+0.47
357.77	18000	14.88	0.375	−0.45

REFERENCES

1 A.B. Teplitsky, I.K. Yanson, O.T. Glukhova, A. Zielenkiewicz, W. Zielenkiewicz and K.L. Wierzchowski, Biophys. Chem., 11 (1980) 17.

2 M. Colomina, P. Jiménez, C. Turrión, J.A. Fernández and C. Monzón, An. Quim., 76A (1980) 245.

3 M. Colomina, P. Jiménez and C. Turrión, J. Chem. Thermodyn., 14 (1982) 779.