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VAPOUR PRESSURES AND ENTHALPIES OF SUBLIMATION OF 1,N^4-DIMETHYL-5-ALKYL DERIVATIVES OF CYTOSINE

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Abstract

The results of determinations of the vapour pressures and enthalpies of sublimation of 1,N^4-dimethyl-5-alkyl derivatives of cytosine are presented.

Keywords: alkylated cytosines, enthalpies of sublimation, vapour pressure

Introduction

Nucleic acid bases are the components of nucleic acids. The knowledge of the hydration process is important for the explanation of their interaction with water and the spatial organization of the polynucleotide chains in aqueous solutions. Thus, the determination of the enthalpy of hydration derived from the experimentally determined the enthalpy of solution, ΔH_{sol}, and the enthalpy of sublimation, ΔH^o_{sub} could be helpful in the elucidation of the nature of these interactions.

In our previous papers we presented the results of determinations of the enthalpies of sublimation for several series differently alkylated uracils [1–5] and adenines [6–9]. In many cases [4, 5, 7, 9] the erratic changes of the enthalpies

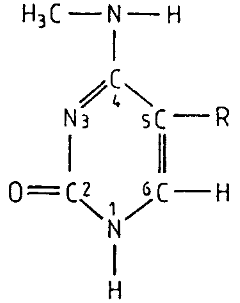

Fig. 1 Structural formula of 1,N^4-dimethyl-5-alkylcytosine R = CH_3, C_2H_5, C_3H_7, C_4H_9

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of sublimation with the elongation of alkyl side chains were observed. It seemed to be interesting to enlarge our investigations on study the alkylated derivatives of cytosine. In this paper the results of investigations of the series of 1,N^4-dimethyl-5-alkyl derivatives of cytosine (Fig. 1) are presented. Owing to the application of Knudsen effusion method it was possible to determine both vapour pressures and enthalpies of sublimation.

Materials

The compounds 1,5,N^4-trimethylcytosine, 1,N^4-dimethyl-5-ethylcytosine, 1,N^4-dimethyl-5-propylcytosine-1,N^4-dimethyl-5-butylcytosine were prepared by individual synthesis and kindly supplied by Dr. Koronkiewicz from University A. Mickiewicz (Poznan, Poland). Their purity, better than 98% was checked using a DuPont Differential Scanning Calorimeter 1090.

Apparatus and procedure

The saturated vapour pressure was measured by the Knudsen effusion method and a set-up identical with that described elsewhere [10]. 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 $6.691\cdot10^{-3}$ 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 thermostat 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

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

where W_a =0.986±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 a least-squares fit to the integrated form of the Clausius-Clapeyron equation, i.e.

$$\log p = -\frac{B}{T} + A$$

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

Results

The results of the measurements of vapour pressures are presented in Table 1, whereas the values of the enthalpies of sublimation, calculated according to the last equation, are collected in Table 2.

Inspection of the values of the enthalpy of sublimation reveals, that in the series of compounds studied elongation of alkyl chain by successive CH_2 groups is first accompanied by an increase in ΔH_{sub} value, then the increment between the two consecutive values is not much bigger than experimental error and fi-

Table 1 Experimental vapour pressure data

T / K	m / mg	t / s	p / Pa
	1,5,N^4-trimethylcytosine		
374.15	1.653	36000	0.0085
376.17	1.791	32400	0.0103
377.16	2.141	36000	0.0111
378.17	2.363	36000	0.0122
381.16	2.714	36000	0.0155
382.15	3.194	36000	0.0166
	1,N^4-dimethyl-5-ethylcytosine		
370.80	1.745	36000	0.0086
371.82	1.920	36000	0.0094
374.07	2.512	36000	0.0124
376.01	2.828	32400	0.0155
376.96	3.458	36000	0.0171
377.89	3.865	36000	0.0191
	1,N^4-dimethyl-5-propylcytosine		
373.97	1.613	36000	0.0076
374.92	1.812	36000	0.0086
375.90	2.047	36000	0.0097
376.98	2.281	36000	0.0108
377.90	2.501	36000	0.0119
378.83	2.799	36000	0.0133
379.81	3.099	36000	0.0148

Table 1 Continued

T / K	m / mg	t / s	p / Pa
	1,N[4]-dimethyl-5-butylcytosine		
372.59	0.819	36000	0.0037
373.79	0.929	36000	0.0042
374.99	1.065	36000	0.0049
375.71	1.131	36000	0.0052
376.41	1.296	36000	0.0059
377.70	1.386	36000	0.0064

T – temperature of measurement; m – mass of the sublimated substance;
t – sublimation time; p – vapour pressure

Table 2 Enthalpy of sublimation of 1,N^4-dimethyl-5-alkyl derivatives of cytosine

Substance	ΔH_{sub}	$\delta\Delta H_{sub}$
	kJ·mol^{-1}	
1,5,N^4-trimethylcytosine	99.18	0.23
1,N^4-dimethyl-5-ethylcytosine	133.44	0.29
1,N^4-dimethyl-5-propylcytosine	132.65	0.22
1,N^4-dimethyl-5-butylcytosine	126.99	0.18

nally decrease for the last member of the series. This character of changes of the increments of ΔH_{sub} indicate on purposefulness of structural, X-ray diffraction study. As it is shown in the paper [11] there exist a good correlation between the values of the enthalpy of sublimation and crystal density and packing energies. Finding such correlation would enrich our considerations.

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Zusammenfassung — Die Ergebnisse der Bestimmung von Gasdruck und Enthalpie der Sublimation von 1,N^4-Dimethyl-5-alkylderivaten von Cytosin werden dargelegt.