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VAPOUR PRESSURES AND SUBLIMATION ENTHALPIES OF THYMINE AND CYTOSINE

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ABSTRACT

The vapour pressures of cytosine and thymine were measured using the torsion-effusion technique. The sublimation processes of cytosine and thymine were investigated over the temperature ranges 480—553 K and 420—503 K, respectively The following pressure—temperature equations were derived by least-squares treatment of the vapour pressure data

cytosine $\log P(\text{kPa}) = 12.48 \pm 0.09 - (7697 \pm 49)/T$

thymine $\log P(\text{kPa}) = 12.79 \pm 0\ 11 - (7016 \pm 51)/T$

The standard sublimation enthalpies were obtained by second- and third-law treatment of the experimental data and the values $\Delta H^0_{298} = 167 \pm 10$ kJ mole^{-1} and $\Delta H^0_{298} = 138 \pm 10$ kJ mole^{-1} were derived for cytosine and thymine, respectively. IR and Raman spectra were recorded in the gas phase in order to evaluate the thermodynamic functions of gaseous cytosine and thymine.

INTRODUCTION

As a continuation of investigations on the vaporization of uracil [1] and its derivatives [2], cytosine and thymine have been considered. The biological properties of these compounds have been investigated in some experimental and theoretical works, e.g. ref. 3. Apparently, no data are reported in the literature concerning thermodynamic functions and, in particular, vapour pressure. We therefore thought it would be useful to study these compounds using the torsion-effusion technique for the vapour measurements and IR and Raman analysis for determination of the thermodynamic functions.

EXPERIMENTAL AND RESULTS

The compounds were supplied by Koch-Light Laboratories and purified by sublimation under vacuum. The purity of the compounds was checked by comparing the experimental melting points with the values reported in the literature: cytosine 538 ± 1 K (539 ± 1 K [4]) and thymine 599 ± 1 K (599 ± 1 K [5]).

Vapour pressure measurements

The torsion-effusion technique and the experimental assembly have been described previously [6,7]. At each temperature, under vacuum, the vapour pressure value was derived from measurements of the torsion angle, α, of the effusion cell, using the well-known relation

$$P(\text{kPa}) = 2\,K\,\alpha/(a_1 l_1 f_1 + a_2 l_2 f_2) = K^0 \alpha$$

where α is the cell deflection, a_1 and a_2 and l_1 and l_2 are the areas of the effusion orifices and their distances from the rotation axis, respectively, f_1 and f_2 and the corresponding geometrical correction factors derived from the equation [8]

$$1/f = 0.0147\,(R/r)^2 + 0.3490\,(R/r) + 0.9982$$

where r and R are the radius and thickness of the effusion hole, respectively. In this study two graphite cells, with geometrical constants $K^0 = (8.21 \pm 0.25)\,10^{-5}$ and $(1.77 \pm 0.25)\,10^{-4}$ kPa deg^{-1}, were employed. The temperatures were measured with a calibrated chromel—alumel thermocouple inserted in a second empty cell placed below the torsion cell. In order to test the temperature measurements and to ensure that the thermodynamic equilibrium existed within the crucible used, the vapour pressure of sulphur was measured. The sublimation enthalpies derived by second- and third-law treatments of the data are in agreement with each other and also with the values selected by Hultgren et al. [9]. The vapour pressures of cytosine and thymine were determined over the temperature ranges 480—553 K and 420—503 K, respectively. The experimental data, obtained as averages of the same values measured at fixed temperatures, are reported in Tables 1 and 2 and plotted in Figs. 1 and 2. The pressure—temperature equations, reported in Table 3 were obtained by least-squares treatment of the data.

Spectroscopic study

The IR spectra of gaseous cytosine and thymine were recorded in the frequency range 100—4000 cm^{-1} using a Perkin-Elmer 180 IR grating spectrophotometer. Details of the experimental apparatus are given in a previous paper [2]. The samples were vaporized under an atmosphere of nitrogen at 760 Torr and 480 K. The Raman spectra were run between 100 and 4000 cm^{-1}, employing the same experimental conditions, using a Cary Raman 81 spectrometer with λ 4358 Å mercury excitation.

Comparison of the IR and Raman spectra of cytosine and thymine indicates that all the normal vibrations are both IR and Raman active according to the activity expectations for molecules of C_s symmetry. This fact can be considered as a diagnostic tool for excluding the presence, in the vapours, of polymeric species as dimers. In fact, the eventual formation of dimers, which are centrosymmetric, should be followed by the appearance in the IR spectra of u-bands and in Raman spectra of g-bands only.

The observed IR and Raman absorptions are listed in Table 4 and their

TABLE 1

Vapour pressures of cytosine determined by the torsion-effusion method

T (K)	No. of points	P (kPa)	$-\Delta[(G^0_T - H^0_{298})/T]$ (J mole K^{-1})	ΔH^0_{298} (kJ mole^{-1})
Run 1				
480	2	2.47×10^{-4}	238.7	166.1
484	2	3.68×10^{-4}	238.65	166.0
486	1	4.11×10^{-4}	238.6	166.1
489	1	4.93×10^{-4}	238.55	166.0
494	4	6.61×10^{-4}	238.5	166.6
497	3	9.04×10^{-4}	238.45	166.6
500	2	1.15×10^{-3}	238.4	166.5
504	3	1.27×10^{-3}	238.35	167.4
507	4	1.64×10^{-3}	238.3	167.0
510	3	2.05×10^{-3}	238.25	167.3
513	4	2.63×10^{-3}	238.2	167.2
517	5	3.24×10^{-3}	238.2	167.6
520	2	3.61×10^{-3}	238.2	168.1
524	3	4.85×10^{-3}	238.15	168.1
527	6	6.31×10^{-3}	238.0	167.8
530	5	7.55×10^{-3}	237.95	167.9
533	5	9.04×10^{-3}	237.85	168.0
537	4	1.24×10^{-2}	237.7	167.8
540	7	1.48×10^{-2}	237.55	167.9
545	8	2.00×10^{-2}	237.4	168.0
548	7	2.51×10^{-2}	237.25	167.2
551	6	3.02×10^{-2}	237.1	167.8
			Average	167.5 ± 0.7 *
Run 2				
496	3	8.45×10^{-4}	238.5	166.5
498	3	1.01×10^{-3}	238.5	166.4
502	4	1.37×10^{-3}	238.4	166.4
506	3	1.86×10^{-3}	238.35	166.4
509	3	2.53×10^{-3}	238.25	166.1
514	4	3.38×10^{-3}	238.2	166.4
516	4	3.89×10^{-3}	238.2	166.5
519	5	4.73×10^{-3}	238.2	166.6
522	4	5.58×10^{-3}	238.15	166.8
524	3	6.43×10^{-3}	238.15	166.5
528	4	8.45×10^{-3}	238.0	166.8
531	4	1.06×10^{-2}	237.95	166.7
534	7	1.35×10^{-2}	237.8	166.4
537	3	1.58×10^{-2}	237.7	166.7
540	4	1.86×10^{-2}	237.55	166.9
543	3	2.06×10^{-2}	237.4	167.2
546	3	2.28×10^{-2}	237.35	167.6
550	4	2.68×10^{-2}	237.15	168.0
553	4	2.89×10^{-2}	236.9	168.5
			Average	166.8 ± 0.5 *

* The errors are the standard deviations.

TABLE 2

Vapour pressure of thymine determined by the torsion-effusion method

T (K)	No. of points	P (kPa)	$-\Delta[(G_T^0 - H_{298}^0)/T]$ (J mole K^{-1})	ΔH_{298}^0 (kJ mole^{-1})
Run 1				
420	2	1.23×10^{-4}	215.1	137.9
425	1	1.64×10^{-4}	215.0	138.5
428	2	2.47×10^{-4}	215.0	138.0
430	1	3.28×10^{-4}	215.0	137.8
433	4	4.11×10^{-4}	215.0	137.8
436	3	4.93×10^{-4}	215.0	138.0
439	4	6.56×10^{-4}	214.9	137.9
441	3	7.40×10^{-4}	214.9	138.1
444	3	1.09×10^{-3}	214.85	137.7
447	3	1.29×10^{-3}	214.85	138.1
450	7	1.415×10^{-3}	214.8	138.5
452	6	1.82×10^{-3}	214.8	138.1
455	3	2.87×10^{-3}	214.8	138.3
458	6	3.36×10^{-3}	214.8	137.6
462	5	5.09×10^{-3}	214.75	137.2
467	5	6.90×10^{-3}	214.75	137.5
471	7	8.22×10^{-3}	214.7	138.0
473	8	9.01×10^{-2}	214.7	138.1
476	6	1.12×10^{-2}	214.65	138.2
479	6	1.42×10^{-2}	214.6	138.1
481	5	1.73×10^{-2}	214.6	137.9
484	5	2.04×10^{-2}	214.6	138.1
			Average	137.9 ± 0.3 *
Run 2				
437	1	7.06×10^{-4}	214.9	137.0
443	2	8.83×10^{-4}	214.9	138.1
447	1	1.06×10^{-3}	214.85	138.6
450	3	1.23×10^{-3}	214.8	139.0
453	2	1.59×10^{-3}	214.8	138.9
457	6	2.30×10^{-3}	214.8	138.8
460	3	3.30×10^{-3}	214.8	138.3
464	7	4.42×10^{-3}	214.75	138.3
467	4	$5\ 75 \times 10^{-3}$	214.75	138.2
469	5	7.58×10^{-3}	214.7	137.7
473	8	9.55×10^{-3}	214.65	138.0
475	5	1.12×10^{-2}	214.65	137.9
478	9	1.39×10^{-2}	214 6	137.9
482	9	1.78×10^{-2}	214.6	138.0
484	8	2.04×10^{-2}	214.6	138.1
487	6	2.51×10^{-2}	214 6	138.1
490	7	3.23×10^{-2}	214.55	137.9
493	7	3.55×10^{-2}	214.55	138.3
496	5	4.36×10^{-2}	214.55	138.3
498	9	5.25×10^{-2}	214.55	138.1
501	5	5.64×10^{-2}	214.55	138.6
503	4	6.17×10^{-2}	214.5	138.8
			Average	138.2 ± 0.4 *

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* The errors are the standard deviations.

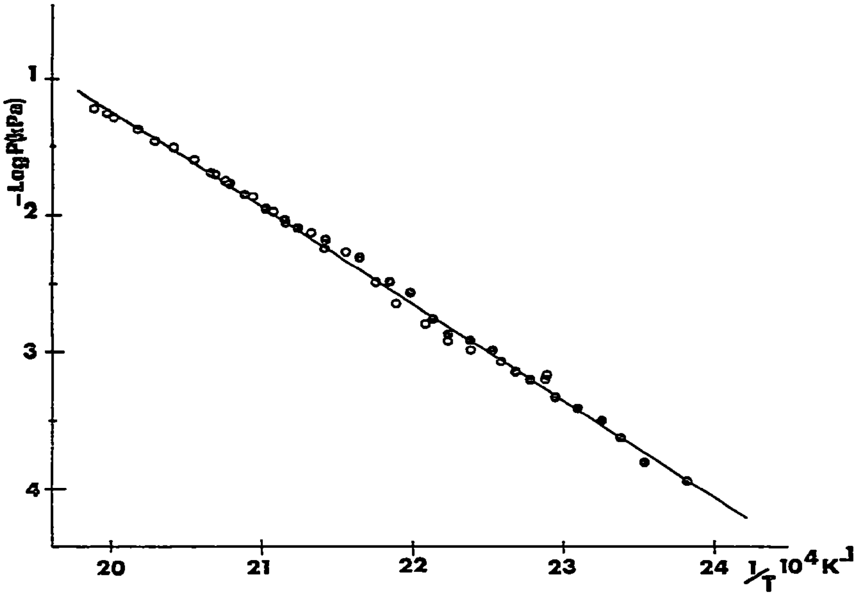

Fig. 1. Vapour pressures of cytosine measured by the torsion-effusion technique. ●, Run 1; ○, run 2.

assignments are considerably aided by analogy with previous assignments of the spectra of solid cytosine [10], uracil [11] and its derivatives [12] and 6-methyl uracil [2]. With regard to the assignment of one of the out-of-plane ring torsions of thymine expected below 100 cm^{-1} in the case of uracil [13], and therefore out of the range of this investigation, we propose the frequency evaluated at 67 cm^{-1} [13].

Calculation of the thermodynamic functions of gaseous thymine and cytosine (reported in Table 5) was carried out employing the well-known methods [14] of statistic mechanics in the approximation rigid-rotator, harmonic oscillator. The rotational and vibrational contributions to the parti-

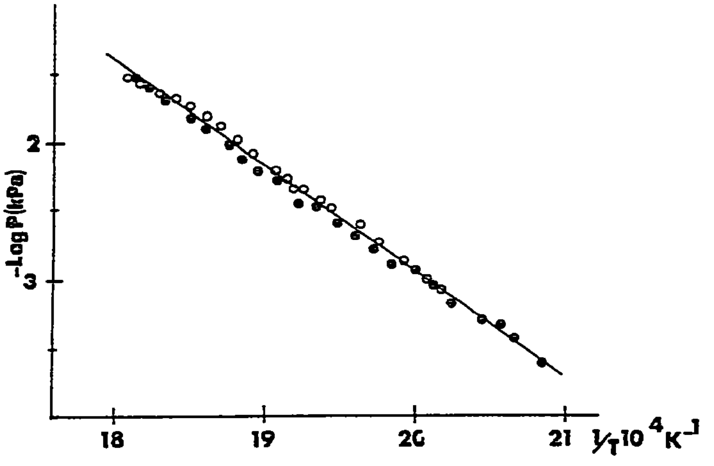

Fig. 2. Vapour pressures of thymine measured by the torsion-effusion technique. ●, Run 1; ○, run 2.

TABLE 3

Vapour pressure—temperature equations of cytosine and thymine

Compound	Run	T (K)	$\log P(\mathrm{kPa}) = A - B/T$	
			A	B
Cytosine	1	480—551	12.75 ± 0.13 *	7755 ± 71 *
	2	496—553	12.37 ± 0.08	7673 ± 40
Thymine	1	420—484	12.54 ± 0.12 *	6896 ± 53 *
	2	437—503	13.05 ± 0.11	7140 ± 50

* The errors are the standard deviations.

TABLE 4

IR and Raman bands of gaseous cytosine and thymine and their assignments

Cytosine		Thymine		Assignment *
IR	Raman	IR	Raman	
3360	3365			$\nu\mathrm{NH_2}$
3249	3253			$\nu\mathrm{NH_2}$
3203	3206	3430	3434	$\nu\mathrm{NH}$
		3402	3407	$\nu\mathrm{NH}$
3107	3112	3021	3020	$\nu\mathrm{CH}$
3096	3100			$\nu\mathrm{CH}$
		2966	2970	$\nu\mathrm{CH_3}$
		2950	2945	
		2938	2931	
1684	1690			$\delta\mathrm{NH_2}$
1661	1666	1720	1722	$\nu\mathrm{CO}$
		1710	1714	$\nu\mathrm{CO}$
1619	1621	1624	1622	$\nu\mathrm{CC}$
1540	1537	1491	1494	$\delta\mathrm{NH}$
1500	1498			$\nu\mathrm{ring}$
		1466	1462	$\delta\mathrm{CH_3}$
		1437	1440	
1458	1460			$\delta\mathrm{CH}$
1351	1360	1421	1425	$\nu\mathrm{CN}$
		1381	1385	$\delta\mathrm{CH_3}$
		1374	1378	$\delta\mathrm{NH}$
		1337	1340	$\delta\mathrm{NH}$
1290	1287			$\delta\mathrm{CH}$
		1269	1271	$\nu\mathrm{CN}$
		1208	1209	$\nu\mathrm{C{-}CH_3}$
1220	1218			$\nu\mathrm{ring}$
		1160	1161	$\delta\mathrm{CH}$
1118	1119			$\nu\mathrm{ring}$
		1064	1066	$\nu\mathrm{CN}$
		1028	1030	$\rho\mathrm{CH_3}$
1040	1042			$\nu\mathrm{ring}$
		1018	1016	$\delta\mathrm{ring}$

TABLE 4 (continued)

Cytosine		Thymine		Assignment *
IR	Raman	IR	Raman	
1000	1004			νring
970	968			νring
		944	947	νCN
		917	920	γCH
827	823			γNH
		808	808	γCO
797	799			νring
780	777			γNH
758	760			γNH
		750	746	νCC
		736	740	γCO
		710	712	γCH
690	692			γNH
		655	658	δC—CH$_3$
630	626			δring
588	590	592	591	skel. def.
570	571	560	559	skel. def.
561	560	540	537	δCO
544	546			δring
522	519			τNH$_2$
		517	515	γC—CH$_3$
		480	481	γNH
		469	465	γNH
450	453			skel. def. O.P.
431	436			skel. def. O.P.
390	392	381	384	δCO
360	363	357		torsion O.P.
		139		torsion O.P.
		67		torsion O.P.

* Frequencies are given in cm^{-1}.
ν = stretching; δ = bending; γ = out-of-plane deformations; ρ = rocking; τ = out-of-plane wagging: skel. def. = skeletal deformation; O.P. = out-of-plane.

tion function were evaluated using the available structural data [15,16] and all the fundamental vibrations reported in Table 4.

The errors associated with each thermodynamic function were calculated assuming the uncertainty of ±2 cm^{-1} in the wave-number values and of ±1° in the bond angles. The electronic statistical weight was kept equal to a singlet $^1\Sigma$, assuming the contribution of the excited electronic levels thoroughly negligible.

CONCLUSIONS

The vapour pressures of cytosine and thymine were measured by the torsion-effusion method and the following pressure—temperature equations

TABLE 5

Thermodynamic functions of gaseous cytosine and thymine

T (K)	S^0_T (J mole K^{-1})	$-(G^0_T - H^0_{298})/T$ (J mole K^{-1})	$H^0_T - H^0_{298}$ (J $mole^{-1}$)
Cytosine			
298.15	337.0 *	337.0 *	0 **
300	337.5	337.2	900
350	354.5	337.9	13810
400	371.0	338.5	13000
450	386.8	342.3	20025
500	403.1	346.9	28100
550	418.2	351.9	36465
Thymine			
298.15	340.0 *	340.0 *	0 **
300	340.5	340.2	90
350	361.8	343.8	6300
400	378.0	347.4	12400
450	395.7	351.0	20415
500	410.0	354.6	27800
550	423.6	358.2	35970

* Uncertainty ± 0.5.

** Uncertainty ± 25.

were obtained

$$\text{cytosine} \log P(\text{kPa}) = (12.48 \pm 0.09) - (7697 \pm 49)/T$$

$$\text{thymine} \log P(\text{kPa}) = (12.79 \pm 0.11) - (7016 \pm 51)/T$$

where the slopes and the intercepts were evaluated weighting the corresponding values obtained in each run (see Table 3), and the associated errors are only the standard deviations. From the vapour pressure data the second-law sublimation enthalpies, $\Delta H_{507} = 147 \pm 1$ kJ $mole^{-1}$ and $\Delta H_{461} = 137 \pm 1$ kJ $mole^{-1}$, were derived for cytosine and thymine, respectively. Third-law sublimation enthalpy values at 298 K were calculated and are reported in Tables 1 and 2 at each experimental temperature; the average values, $\Delta H^0_{298} = 167 \pm 1$ kJ $mole^{-1}$ and $\Delta H^0_{298} = 138 \pm 1$ kJ $mole^{-1}$, for cytosine and thymine, respectively, are in very good agreement with the values $\Delta H^0_{298} = 166 \pm 1$ kJ $mole^{-1}$ and $\Delta H^0_{298} = 137 \pm 1$ kJ $mole^{-1}$. The reductions to 298 K of the reported ΔH_T were made by interpolating the heat content functions $(H^0_T - H^0_{298})$ (g) $-$ $(H^0_T - H^0_{298})$ (s) (see Table 5 and ref. 1). The necessary free-energy functions $-(G^0_T - H^0_{298})/T$ and the heat contents of solid cytosine and thymine, were evaluated assuming the heat capacities of cytosine to be equal to those of uracil [1] corrected for the difference $[C_p(NH_2) - \{C_p(O) + C_p(H)\}]$ [17] and those of thymine to be equal to the heat capacities of 6-methyluracil [2]. The thermodynamic functions for the gaseous phases are those calculated in this work. The very good agreement between second- and third-law sublimation enthalpy values leads us to associate an error inferior to 10 kJ $mole^{-1}$ in the ΔH^0_{298} values, also taking into account the uncertainties in the estimation of the thermodynamic functions. We therefore propose values of $\Delta H^0_{298} = 167 \pm 10$ kJ mole^{-1} and $\Delta H^0_{298} = 138 \pm 1$ kJ mole^{-1} for the sublimation energies of cytosine and thymine, respectively.

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