Sublimation Enthalpies of Some Methyl Derivatives of Uracil from Vapor Pressure Measurements

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The standard sublimation enthalpies for uracil, 1-methyluracil, 3-methyluracil, and 1,3-dimethyluracil, $\Delta_{sub}H^{\circ}$(298 K) = (128 ± 2), (124 ± 5), (121 ± 4), and (118 ± 4) kJ mol^{-1}, respectively, were determined from their vapor pressures measured by the torsion method. The results of vapor pressure measurements were fit to the following linear equations: uracil, $\log(p/\text{kPa}) = (12.29 \pm 0.15) - (6634 \pm 100)$ K/T (from 384 K to 494 K); 1-methyluracil, $\log(p/\text{kPa}) = (13.75 \pm 0.15) - (6357 \pm 150)$ K/T (from 343 K to 428 K); 3-methyluracil, $\log(p/\text{kPa}) = (13.59 \pm 0.10) - (6210 \pm 100)$ K/T (from 344 K to 419 K); 1,3-dimethyluracil, $\log(p/\text{kPa}) = (15.10 \pm 0.10) - (6049 \pm 100)$ K/T (from 311 K to 364 K). The different sublimation behavior of some compounds can be due to the presence of hydrogen bonds in their solid state.

Introduction

As part of a program on the study of the vaporization of organic compounds, the sublimation enthalpies of 1-methyluracil (1-mU), 3-methyluracil (3-mU), and 1,3-dimethyluracil (1,3-dmU) were determined by measuring their vapor pressures by the torsion method. Very few thermodynamic data associated with the vaporization of these methyl derivatives of uracil have appeared in the literature until now. In particular for 3-mU, the only sublimation enthalpy found in the literature is the Knudsen value reported by Romanov et al. (1972). For 1,3-dmU, in addition to an early spectroscopic sublimation enthalpy value reported by Clark et al. (1965), the Knudsen value (Romanov et al., 1972) and another one determined by Yanson et al. (1979) by the resonator method are apparently the only enthalpy values found in the literature. For 1-mU, neither the vapor pressure nor the sublimation enthalpy of this compound was found. In the present work the vapor pressure and sublimation enthalpy of uracil (U) were also measured in order to compare the vaporization behavior of this compound with those of its methyl derivatives. It is believed that the sublimation enthalpy value for U obtained spectrometrically by Clark et al. (1965) is not reliable because of the temperature dependence of the total intensity of UV spectra of bases in the gaseous phase. The sublimation enthalpy reported by Romanov et al. (1972) was obtained using the classical Knudsen method; sublimation enthalpies were also determined by Yanson et al. using a quartz resonator method (Yanson et al., 1974) and a mass spectrometer (Yanson et al., 1979). In the last paper it is reported that a very small amount (<1%) of the dimer form was also present in the vapor phase. The sublimation of U was calorimetrically studied by Nabavian et al. (1977). Also the vapor pressure of U was measured by torsion, Knudsen, and transpiration methods by Bardi et al. (1980) and, when the obtained data are treated by the second and third laws, a new sublimation enthalpy of this compound was determined. Unfortunately, the several sublimation enthalpy values of U reported in the literature (see Table 3) were not in agreement.

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Experimental Section

U (98% pure), 1-mU (99% pure), 3-mU (98% pure), and 1,3-dmU (99% pure) were supplied by Sigma Chemical Co, with the purities certified by the supplier.

The vapor pressures of these substances were determined by the torsion assembly described in a previous work (Piacente et al., 1994). A conventional graphite torsion cell with compartments having different areas of their effusion holes (0.5 and 1.8 mm in the diameter) was used in this study in order to measure vapor pressures in a large temperature range and in the same experimental condition. In fact, when both compartments are filled with a compound, the torsion of the assembly is produced by the effusion of the vapor from both compartments (cell A). Because the vapor effuses in a greater amount from the compartment with the larger effusion hole than from the other one, the sample filled in this lodging vaporizes more rapidly. When all of the sample in this compartment is completely vaporized, the torsion angle decreases decidedly and its new value is due to the effusion of the vapor from the other compartment with the small effusion hole. Now, the cell behaves as a new cell (cell B), so that when the temperature is increased, it is possible to measure a new vapor pressure set at higher temperatures. In this way two vapor pressure sets were measured at two temperature ranges in the same experimental conditions. In Figure 1 a typical plot of the torsion data obtained by using this cell as cell A and cell B is reported. During the vapor pressure measurements at some temperatures, the molecular weight of the vapor of the studied compound was also determined by the Knudsen equation (Knudsen, 1909) by measuring the mass loss rate of the sample by a vacuum balance (Cahn 1000), to which is suspended the torsion assembly. The cell constants necessary to convert both the torsion angle in pressure and the mass loss rate in molecular weight were determined in the usual way by vaporizing very pure standards having well-known vapor pressure [cadmium (Hultgreen et al., 1973); benzoic acid (Colomina et al., 1982)]. The cell constant values measured in runs carried out before and after each vaporization run were practically equal or different by no more than 5% of their average value. This value was used for treating the
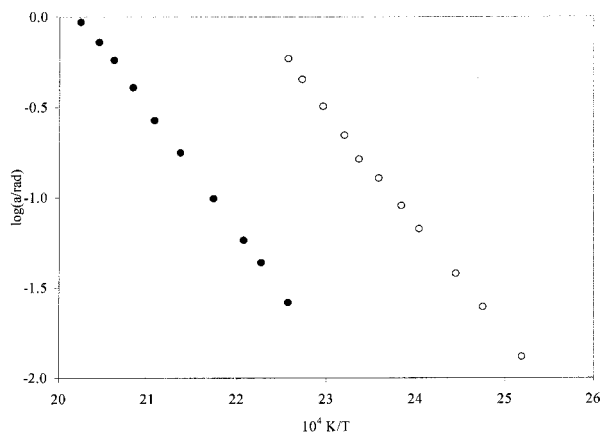
Figure 1. Torsion angles obtained by vaporizing uracil (run 14) using the torsion cell as cell A (○) and cell B (●).

Table 1. Vapor Pressure of Uracil by Torsion Measurements

	run 2			run 6			run 14	
cell	T/K	$-\log(p/\text{kPa})$	cell	T/K	$-\log(p/\text{kPa})$	cell	T/K	$-\log(p/\text{kPa})$
A	387.0	4.84	A	384.0	5.07	A	397.0	4.36
	391.0	4.62		391.5	4.67		404.0	4.09
	395.0	4.42		396.0	4.47		409.0	3.90
	399.0	4.32		399.5	4.29		416.0	3.66
	406.0	4.02		402.0	4.22		419.5	3.53
	412.0	3.79		406.5	4.07		424.0	3.37
	416.0	3.62		410.5	3.92		428.0	3.27
	428.0	3.20		416.5	3.67		431.0	3.14
				421.5	3.50		435.5	2.98
B	428.0	3.16		425.0	3.35		440.0	2.83
	449.0	2.46		429.5	3.20		443.0	2.71
	458.5	2.16		433.5	3.04			
	467.0	1.90				B	443.0	2.68
	472.0	1.77	B	437.0	2.86		449.0	2.46
	478.0	1.62		439.0	2.83		453.0	2.34
	487.0	1.33		444.0	2.74		460.0	2.11
	492.0	1.18		449.0	2.49		468.0	1.85
				453.0	2.40		474.5	1.67
				457.0	2.27		480.0	1.49
				461.0	2.13		485.0	1.34
				465.5	1.98		489.0	1.24
				469.5	1.87		494.0	1.13
				474.0	1.72			
				479.0	1.57			
				494.0	1.15			

experimental data measured in that run. The uncertainties associated with the torsion angle measurements and with the cell constant should produce a displacement of the log p of no larger than ± 0.03. The uncertainty associated with the temperature, as evaluated by breaking the vapor pressure of cadmium at the melting point, could be about 2 K.

The vapor pressure of uracil, reported in Table 1 and given in Figure 2, is decidedly in excellent agreement. For each run the corresponding pressure equation as obtained by treating the experimental data by a linear least-squares method is reported in Table 2.

The equation

$$\log(p/\text{kPa}) = (12.29 \pm 0.15) - (6634 \pm 100)\ \text{K}/T \quad (1)$$

was obtained by weighting the slope and intercept of each pressure equation proportionally to the number of the experimental points where this equation was selected as representative of the vapor pressure of uracil in the temperature range (384 K to 494 K), where the errors were
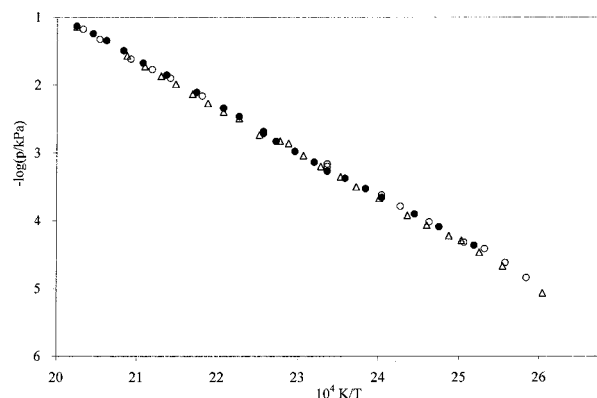

Figure 2. Vapor pressures of uracil: ○, run 2; △, run 6; ●, run 14.

estimated. This equation was compared with the results reported by Bardi et al. (1980) in Table 3.

The vapor pressures of 1-mU, 3-mU, and 1,3-dmU are reported in Tables 4−6 and in Figures 3−5. For each vaporization run the linear regression of the logarithm of the pressure as a function of the reciprocal temperature was calculated by a least-squares method. Table 2 gives the equations so obtained together with the covered temperature ranges. From these equations the following equations are selected:

1-mU
$$\log(p/\text{kPa}) = (13.75 \pm 0.15) - (6357 \pm 150)\ \text{K}/T$$
$$\text{(from 343 K to 428 K)} \quad (2)$$

3-mU
$$\log(p/\text{kPa}) = (13.59 \pm 0.10) - (6210 \pm 100)\ \text{K}/T$$
$$\text{(from 344 K to 419 K)} \quad (3)$$

1,3-dmU
$$\log(p/\text{kPa}) = (15.10 \pm 0.10) - (6049 \pm 100)\ \text{K}/T$$
$$\text{(from 311 K to 364 K)} \quad (4)$$

where errors associated with slopes and intercepts were estimated.

Discussion and Conclusion

The temperature dependencies of the vapor pressures for U, 1-mU, 3-mU, and 1,3-dmU measured in the present paper are represented by eqs 1−4. Considering these vaporizations of the compounds to be congruent, as confirmed from the molecular weight value of the vapor determined by the Knudsen method during the vapor pressure measurements, from the slopes of these equations the sublimation enthalpies referred to the mean temperatures of the ranges over which measurements were calculated. The obtained values are reported in Table 3.

Concerning uracil, the sublimation enthalpy $\Delta_{\text{sub}}H^\circ(439\text{ K}) = (127.0 \pm 2)$ kJ mol^{-1} is in excellent agreement with that calorimetrically measured by Nabavian (1977) at the same temperature, $\Delta_{\text{sub}}H^\circ(400\text{ K}) = (126.5 \pm 2.2)$ kJ mol^{-1}. This value was reported at 298 K by the heat contents for solid and gaseous phases found in Bardi's paper, $\Delta_{\text{sub}}H^\circ(298\text{ K}) = (130.0 \pm 2.0)$ kJ mol^{-1}. The standard sublimation enthalpy of U was also calculated by the third law at 400 and 500 K, approximate extreme experimental temperatures, using the pressures from eq 1 and the change of the free energy functions, $\Delta[(G^\circ(T) - H^\circ(298\text{ K}))/T] = 195$ and 194 J K^{-1} mol^{-1} at 400 and 500 K, respectively, from the same source of the heat contents. The obtained values,

Table 2. Temperature Dependence of the Vapor Pressures of Uracil and of Its Methyl Derivatives

				$\log(p/\text{kPa}) = A - B/(T/\text{K})$	
compound	run	$\Delta T/\text{K}$	no. of points	A^a	B^a
uracil	2	387−492	16	12.12 ± 0.07	6552 ± 30
	6	384−494	24	12.31 ± 0.08	6652 ± 109
	14	397−494	21	12.39 ± 0.11	6676 ± 50
1-methyluracil	3	343.5−425	19	13.59 ± 0.10	6293 ± 39
	7	355−428	13	13.97 ± 0.26	6452 ± 99
3-methyluracil	5	344.5−419	20	13.61 ± 0.07	6219 ± 27
	12	369−419	11	13.54 ± 0.15	6193 ± 60
1,3-dimethyluracil	9	311−364	17	15.16 ± 0.14	6070 ± 48
	15	337−364	11	15.01 ± 0.21	6017 ± 73

^{a} The errors are the standard deviations.

Table 3. Comparison of the Temperature Dependence of the Total Vapor Pressures and Sublimation Enthalpies for Uracil, 1-Methyluracil, 3-Methyluracil, and 1,3-Dimethyluracil

					$\log(p/\text{kPa}) = A - B/T$	
compound	ref	method	T/K	$\Delta H^\circ \,(T)/(\text{kJ mol}^{-1})$	A	B
uracil	Clark et al. (1965)	mass spectrometer	≈485	84		
	Romanov et al. (1972)	Knudsen	?	115.5 ± 2.1		
	Yanson et al. (1974)	quartz resonator	418	120.5 ± 5.2		
	Yanson et al. (1979)	mass spectrometer	425	121.7		
	Nabavian et al. (1977)	calorimeter	440	126.5 ± 2.2		
	Bardi et al. (1980)	torsion, Knudsen, transpiration	519	130.6 ± 4.0	12.13 ± 0.50	6823 ± 210
	this work	torsion	439	127.0 ± 2.0	12.29 ± 0.15	6634 ± 100
1-methyluracil	this work	torsion	386	121.7 ± 4.0	13.75 ± 0.15	6357 ± 150
3-methyluracil	Romanov et al. (1972)	Knudsen	?	69.5 ± 1.2		
	this work	torsion	382	118.8 ± 3.0	13.59 ± 0.10	6210 ± 100
1,3-dimethyluracil	Clark et al. (1965)	mass spectrometer	≈357	92		
	Romanov et al. (1972)	Knudsen	?	77.0 ± 1.2		
	Yanson et al. (1979)	quartz resonator	?	101.7 ± 2.5		
	this work	torsion	338	115.8 ± 3.0	15.10 ± 0.10	6049 ± 100

Table 4. Vapor Pressure of 1-Methyluracil by Torsion Measurements

	run 3			run 7	
cell	T/K	$-\log(p/\text{kPa})$	cell	T/K	$-\log(p/\text{kPa})$
A	343.5	4.77	A	355.0	4.21
	345.5	4.62		358.5	3.99
	348.0	4.51		368.0	3.58
	349.0	4.39		373.0	3.33
	351.0	4.29		378.0	3.09
	358.0	3.96		381.5	2.93
	364.0	3.72		384.5	2.84
	368.0	3.50		389.5	2.71
	374.0	3.23			
	376.5	3.12	B	387.0	2.62
	382.0	2.89		396.0	2.29
				407.5	1.91
B	391.0	2.44		419.5	1.37
	396.5	2.29		428.0	1.10
	401.0	2.12			
	406.5	1.93			
	410.5	1.75			
	415.0	1.59			
	420.5	1.34			
	425.0	1.18			

Table 5. Vapor Pressure of 3-Methyluracil by Torsion Measurements

	run 5			run 12	
cell	T/K	$-\log(p/\text{kPa})$	cell	T/K	$-\log(p/\text{kPa})$
A	344.5	4.47	A	340.0	4.69
	351.0	4.13		346.0	4.39
	355.5	3.87		351.5	4.02
	359.0	3.71		356.5	3.75
	362.0	3.56		360.5	3.60
	365.0	3.42		365.5	3.38
	368.0	3.29		370.0	3.16
	371.5	3.13		375.5	2.90
	375.5	2.94		379.5	2.79
B	369.0	3.24	B	385.5	2.49
	375.5	2.94		395.5	2.14
	380.0	2.74		401.0	1.89
	383.0	2.64		405.5	1.76
	390.5	2.32		410.0	1.53
	396.0	2.11		415.0	1.33
	402.0	1.91		419.5	1.20
	407.0	1.68			
	410.5	1.53			
	414.5	1.37			
	419.0	1.23			

$\Delta_{\text{sub}}H^\circ(298 \text{ K}) = 126.2$ and $125.6 \text{ kJ mol}^{-1}$ at 400 and 500 K, respectively, show a decidedly negligible temperature trend, and their average value ($125.9 \text{ kJ mol}^{-1}$) agrees enough with our second-law result and that selected by Bardi et al. (1980) [$\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (131 \pm 5) \text{ kJ mol}^{-1}$]. Taking into account these results, we believe that the more reliable value for the standard sublimation enthalpy of U is $(128 \pm 2) \text{ kJ mol}^{-1}$.

Concerning the alkyl derivatives, in the absence of values for Cp for these compounds in the solid and gaseous phases, it is not possible to calculate accurately the standard sublimation enthalpies from the enthalpy values $\Delta_{\text{sub}}H^\circ$-$(386 \text{ K}) = (121.7 \pm 4.0)$, $\Delta_{\text{sub}}H^\circ(382 \text{ K}) = (118.8 \pm 3.0)$, and

$\Delta_{\text{sub}}H^\circ(338 \text{ K}) = (115.8 \pm 3.0) \text{ kJ mol}^{-1}$ for 1-mU, 3-mU, and 1,3-dmU, respectively; considering that the mean temperatures are near enough to 298 K, for correcting the enthalpic values an increment of about 2 kJ mol^{-1} was estimated for all compounds, an increment of the same magnitude as that of U (Bardi et al., 1980). The standard sublimation enthalpies $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (124.0 \pm 5)$, (121 ± 4), and $(118 \pm 4) \text{ kJ mol}^{-1}$ were derived for 1-mU, 3-mU, and 1,3-dmU, respectively, where the errors were overestimated for the systematic errors in the temperature readings, for the uncertainties in the measurements of the low torsion angles, and for the corrections of the sublima-
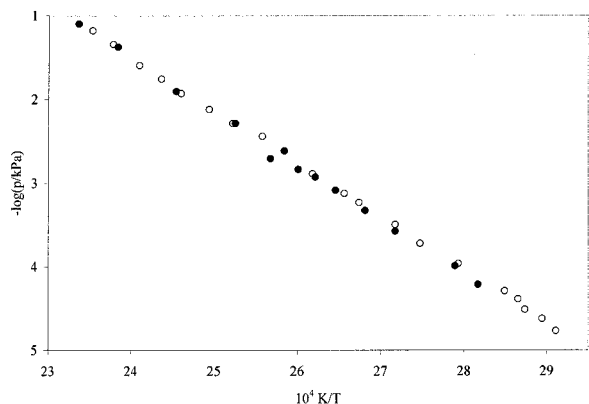
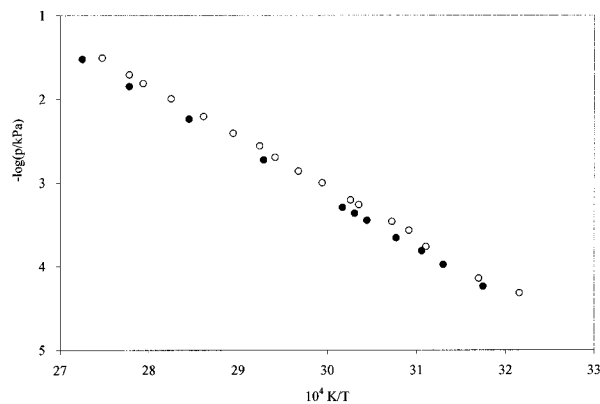**Figure 3.** Vapor pressures of 1-methyluracil: ○, run 3; ●, run 7.

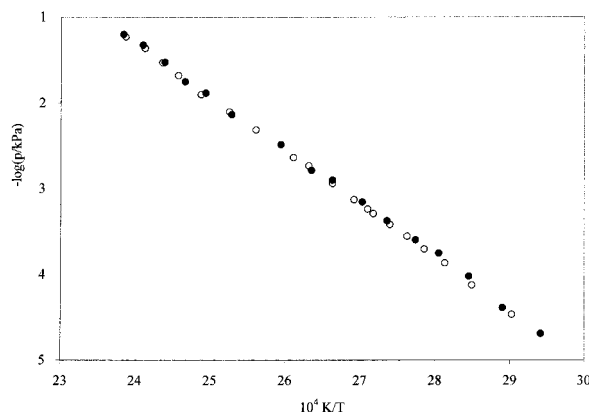**Figure 4.** Vapor pressures of 3-methyluracil: ○, run 5; ●, run 12.

Figure 5. Vapor pressures of 1,3-dimethyluracil: ○, run 9; ●, run 15.

Figure 6. Vapor pressures of uracil (A), 1-methyluracil (B), 3-methyluracil (C), 1,3-dimethyluracil (D), and 6-methyluracil (E).

Table 6. Vapor Pressure of 1,3-Dimethyluracil by Torsion Measurements

	run 9			run 15	
cell	T/K	$-\log(p/kPa)$	cell	T/K	$-\log(p/kPa)$
A	311.0	4.32	A	315.0	4.24
	315.5	4.14		319.5	3.98
	321.5	3.76		322.0	3.81
	323.5	3.57		325.0	3.66
	325.5	3.46		328.5	3.45
	329.5	3.26		330.0	3.36
	330.5	3.21		331.5	3.29
	334.0	3.00			
	340.0	2.69	B	341.5	2.73
				351.5	2.24
B	337.0	2.86		360.0	1.85
	342.0	2.56		367.0	1.53
	345.5	2.41			
	349.5	2.21			
	354.0	1.99			
	358.0	1.81			
	360.0	1.71			
	364.0	1.51			

tion enthalpies at 298 K. In Figure 6 are given the selected pressure–temperature equations for U, 1-mU, 3-mU, and 1,3-dmU, and for 6-methyluracil (6-mU), previously determined in our laboratory (Ferro et al., 1980), $\log(p/kPa) = (12.09 \pm 0.07) - (6652 \pm 34)$ K$/T$. A vision of the vaporization behaviors of these compounds shows that, whereas their sublimation enthalpies are comparable, even with a small trend from U to 1,3-dmU, the standard free energies, $\Delta_{sub}G°$ (T), associated with the sublimation processes, connected with the absolute vapor pressures, are different. For 6-mU (U C-methyl substituted) the sublimation $\Delta_{sub}G°(T)$ is comparable with that of U, while for 1-mU and 3-mU (both U N-methyl substituted) the standard free
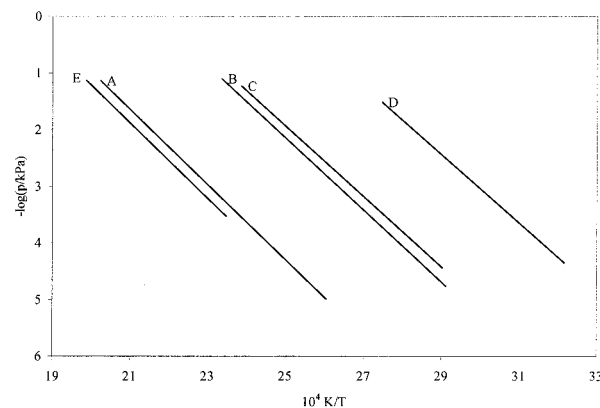
energies are smaller than that of U, with the smallest being 1,3-dmU. These observations and the small trend observed in $\Delta_{sub}H°(298\ K)$ values could be explained by the crystal structures of these compounds. In fact, 1,3-dmU is unable to form conventional hydrogen bonds in the solid state (Banerjee et al., 1977) while U displays a three-dimensional pattern of intermolecular hydrogen bonds of increasing complexity associated with the availability of the N–H groups (Stewart and Jensen, 1967; Portalone et al., 1999) so that these compounds present a more physical stability. For 1-mU (McMullan and Craven, 1989), less associated in the crystal, the vaporization behavior is intermediate between U and 1,3-dmU.

Literature Cited

Banerjee, A.; Dattagupta, J. K.; Saenger, W.; Rabczenuko, A. 1,3-Dimethyluracil: A Crystal Structure Without Hydrogen Bonds. *Acta Crystallogr.* **1977**, *B33*, 90–94.

Bardi, G.; Bencivenni, L.; Ferro, D.; Martini, B.; Nunziante Cesaro, S. Teghil, R. Thermodynamic Study of the Vaporization of Uracil. *Thermochim. Acta* **1980**, *40*, 275–282.

Clark, L. B.; Peschel, G. G.; Tinoco, I. Vapor Spectra and Heats of Vaporization of Some Purine and Pyrimidine Bases. *J. Phys. Chem.* **1965**, *69* (10), 3615–3618.

Colomina, M.; Jimenez, P.; Turrion, C. Thermochemical Properties of Benzoic Acid Derivatives. *J. Chem. Thermodyn.* **1982**, *14*, 779.

Ferro, D.; Bencivenni, L.; Teghil, R.; Pelino, M. Thermodynamic and Spectroscopic Study of 6-Methyluracil. *J. Indian Chem. Soc.* **1980**, *57*, 629–632.

Hultgreen, R.; Desai, P. D.; Hawkins, D. T.; Gleiserand, M.; Kelley, K. K. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metals Park, OH, 1973.

Knudsen, M. Effusion and the Molecular Flow of Gases Through Openings *Ann. Phys.* **1909**, *29*, 179.

McMullan, R. K.; Craven, B. M. Crystal Structure of 1-Methyluracil from Neutron Diffraction at 15, 60 and 123 K. *Acta Crystallogr.* **1989**, *B45*, 270–276.

Nabavian, M.; Sabbah, R.; Chastel, R.; Laffitte, M. Thermodynamic of Nitrogen Compounds. *J. Chim. Phys.* **1977**, *74* (1), 115−126.

Piacente, V.; Fontana, D.; Scardala, P. Enthalpies of Vaporization of a Homologous Series of *n*-Alkanes Determined from Vapor Pressure Measurements. *J. Chem. Eng. Data* **1994**, *39*, 231−237.

Portalone, G.; Bencivenni, L.; Colapietro, M.; Pieretti, A.; Raimondo, F. The effect of Hydrogen Bonding on the Structures of Uracil and some Methylderivatives Studied by Experiment and Theory. *Acta Chem. Scand.* **1999**, *53*, 57−68.

Romanov, B. C.; Sukkhorukov, B. I.; Miroshnichenko, E. A.; Lebedev, Yu. A. *Fourth Int. Biophys. Congr. Abstr.* **1972**, *E7* (a4/7).

Stewart, R. F.; Jensen, L. H. Redetermination of the Crystal Structure of Uracil. *Acta Crystallogr.* **1967**, *23*, 1102−1105.

Yanson, I. K.; Verkin, B. I.; Shklyarevsky, O. I.; Teplitsky, A. B. Sublimation Heats of Nitrogen Bases of Nucleic Acids. *Stud. Biophys.* **1974**, *46*, 29−44.

Yanson, I. K.; Teplitsky, A. B.; Sukhodub, L. F. Experimental Studies of Molecular Interactions Between Nitrogen Bases of Nucleic acids. *Biopolymers* **1979**, *18*, 1149−1170.