

Vapour pressures and sublimation enthalpies of urea and some of its derivatives

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(Received 12 June 1986; in final form 5 January 1987)

The sublimation enthalpy and entropy of urea and its derivatives monomethylurea (MMU), monoethylurea (MEU), monopropylurea (MPU), dimethyl-1,1-urea (1,1-DMU), dimethyl-1,3-urea (1,3-DMU), and diethyl-1,3-urea (1,3-DEU) were determined from the dependence of their vapour pressures on temperature. The vapour pressures were measured by the torsion-effusion method. The corresponding pressure against temperature equations are: urea, $\lg(p/\text{kPa}) = 10.30 - 4750(\text{K}/T)$; MMU, $\lg(p/\text{kPa}) = 10.72 - 4562(\text{K}/T)$; MEU, $\lg(p/\text{kPa}) = 10.20 - 4496(\text{K}/T)$; MPU, $\lg(p/\text{kPa}) = 10.83 - 4608(\text{K}/T)$; 1,1-DMU, $\lg(p/\text{kPa}) = 11.13 - 4655(\text{K}/T)$; 1,3-DMU, $\lg(p/\text{kPa}) = 10.78 - 4454(\text{K}/T)$; 1,3-DEU, $\lg(p/\text{kPa}) = 12.20 - 5047(\text{K}/T)$; where the errors associated with the slopes (± 100) and intercepts (± 0.18), (± 0.30 for urea), were estimated.

1. Introduction

Reliable results on the vaporization enthalpy changes of pure substances are of great interest in various thermodynamic fields because they provide information about the physical and chemical stabilities of the substances studied and permit one to derive, from appropriate cycles, other thermodynamic information useful for theoretical studies on the condensed phases or for practical applications.

As part of our recent programme on the vaporization study of pure organic compounds,^(1,2) the enthalpy changes associated with the sublimation of urea and some of its mono- and di-substituted derivatives were determined by vapour-pressure measurements. The vaporization enthalpies may be combined with the enthalpies of solution at infinite dilution to give solvation or hydration enthalpies.^(3–5) These quantities are of primary importance for a quantitative treatment of solute–solvent interactions in water and in organic solvents.^(3–6) From this point of view, the vaporization studies on urea and its derivatives (that are of interest for biochemistry) are promising because other thermodynamic properties of these compounds continue to be determined in water^(7–11) and in mixed solvents.^(12,13)

For urea, a significant difference exists between the $\Delta_{\text{sub}}H_m^\circ(T)$ found by Suzuki *et al.*⁽¹⁴⁾ and Ritter Sutter⁽¹⁵⁾ and the values reported by Trimble and Voorhoeve⁽¹⁶⁾ and De Wit *et al.*⁽¹⁷⁾ Apparently no enthalpies of sublimation have been determined for its derivatives: monomethylurea (MMU), monoethylurea (MEU), monopropylurea (MPU), dimethyl-1,1-urea (1,1-DMU), dimethyl-1,3-urea (1,3-DMU), and diethyl-1,3-urea (1,3-DEU).

The vapour pressures and the corresponding sublimation enthalpy and entropy changes of these compounds derived from a second-law treatment of the experimental vapour pressure are reported in this work.

2. Experimental

The chemicals used were first-grade purity (>98 mass per cent) commercial products from Aldrich, but *n*-propylurea was from Kodak. All products were purified by several (up to five) recrystallizations from ethyl acetate (for urea only, ethanol was used as solvent). Final purities were checked by enthalpy of fusion thermograms (d.s.c. 111-Setaram) and by g.c. and can be assumed to be better than 99.9 mass per cent for all samples submitted to measurements.

Vapour pressures were measured by a torsion-effusion assembly. The method and assembly employed have been described previously.^(18,19) Pressures were determined from the torsion angle α of the tungsten wire (30 μm in diameter), from which the cell was suspended, using the relation: $p = 2K\alpha/(a_1l_1f_1 + a_2l_2f_2)$ where a_1 , a_2 and l_1 , l_2 are the areas of the effusion orifices and their distances from the rotation axis, and f_1 and f_2 are the geometrical factors⁽²⁰⁾ derived from the equation: $1/f = 0.9882 + 0.3490(R/r) + (R/r)^2$, where r and R are the radius and the thickness respectively of the effusion orifice. The vaporizations were carried out with graphite and pyrophyllite cells with different diameter and thickness of the effusion holes. The geometrical constants of the cells are reported in table 1. To verify that the temperature measurements were reliable and that equilibrium was achieved in the cell, the pressure of pure naphthalene was measured as standard. The results agreed (within about 15 per cent) with those selected by Colomina *et al.*⁽²¹⁾

TABLE 1. Constants of the torsion-effusion cells; K for the tungsten wire is $(2.0 \pm 0.2) \times 10^{-6} \text{ N} \cdot \text{m}$

Cell	Material	Orifice area ($\pm 0.05 \times 10^3 \text{ cm}^2$) ^a		Moment arm ($\pm 0.05 \text{ cm}$)		Freeman-Searcy factor ⁽²⁰⁾	
		a_1	a_2	l_1	l_2	f_1	f_2
A	graphite	7.85	9.50	0.50	0.53	0.57	0.59
B	pyrophyllite	11.30	10.32	0.57	0.63	0.32	0.56
C	graphite	3.32	4.53	1.02	1.05	0.60	0.47
D	pyrophyllite	5.03	4.83	1.46	1.46	0.48	0.50
D1	graphite	4.42	5.28	0.52	1.48	0.47	0.40
H	pyrophyllite	9.50	10.20	0.67	0.63	0.59	0.49
X	pyrophyllite	6.36	5.81	0.52	0.50	0.44	0.50

^a Measured by photographic enlargement.

3. Results

The vapour pressure of urea was determined in six runs in the overall temperature range 354 to 409 K employing four different cells. The experimental results are plotted in figure 1 and the $p(T)$ equations, obtained from a least-squares treatment for each run, are in table 2. By weighting slopes and intercepts in proportion to the experimental points the following equation was selected:

$$\lg(p/\text{kPa}) = (10.30 \pm 0.30) - (4750 \pm 100)(\text{K}/T), \quad (1)$$

where the associated errors are estimated on the basis of the uncertainties of the temperature measurements and of the cell calibration constants. The equation plotted in figure 2 for comparison with the literature shows that the vapour pressures are in general agreement.

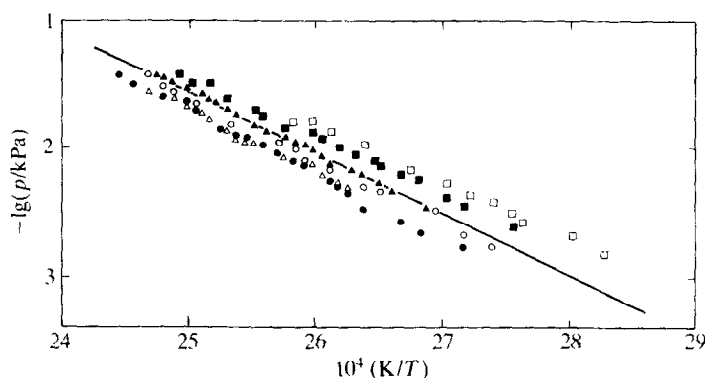


FIGURE 1. Experimental vapour pressure of urea. \circ , Run D01; \bullet , Run D02; \triangle , Run D04; \blacktriangle , Run D08; \square , Run 626; \blacksquare , Run 821.

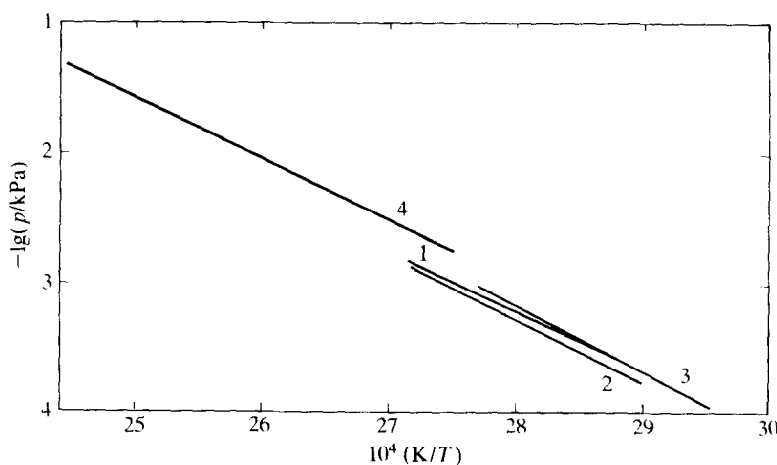


FIGURE 2. Vapour pressure of urea. 1, Suzuki *et al.*;⁽¹⁴⁾ 2, Trimble and Voorhoeve;⁽¹⁶⁾ 3, De Wit *et al.*;⁽¹⁷⁾ 4, this work.

TABLE 2. Coefficients of $p(T)$ equations $\lg(p/\text{kPa}) = A - B(K/T)$ for urea and its derivatives; N points between T_1 and T_2 ; the uncertainties of A and B are standard deviations

Compound	Run	Cell	T_1/K T_2/K	N	A	B
urea	D01	D	365 to 405	14	10.37 ± 0.18	4798 ± 71
	D02	D1	368 to 409	19	10.23 ± 0.14	4776 ± 56
	D04	D1	381 to 405	15	10.66 ± 0.30	4938 ± 120
	D08	D	372 to 404	22	10.99 ± 0.16	5018 ± 64
	626	X	354 to 385	11	9.58 ± 0.15	4385 ± 58
	821	A	363 to 401	18	9.60 ± 0.15	4430 ± 59
MMU	328	H	327 to 371	17	10.45 ± 0.10	4478 ± 32
	330	C	326 to 364	10	10.33 ± 0.14	4431 ± 50
	D26	D	353 to 371	9	11.66 ± 0.23	4866 ± 83
MEU	323	H	333 to 363	16	9.72 ± 0.10	4306 ± 38
	327	C	327 to 360	13	10.87 ± 0.17	4660 ± 47
	D28	D	358 to 365	8	10.69 ± 0.69	4608 ± 25
MPU	606	X	336 to 368	13	9.91 ± 0.27	4283 ± 96
	611	C	332 to 370	11	11.17 ± 0.21	4728 ± 76
	D29	D	352 to 373	11	11.58 ± 0.12	4873 ± 37
1,1-DMU	829	A	326 to 364	10	11.16 ± 0.20	4656 ± 68
	903	A	329 to 369	14	11.83 ± 0.10	4909 ± 36
	D11	D	329 to 369	15	10.46 ± 0.14	4418 ± 49
1,3-DMU	820	A	316 to 366	11	11.02 ± 0.11	4520 ± 36
	821	A	323 to 358	7	11.46 ± 0.11	4693 ± 36
	D06	D	326 to 373	16	10.31 ± 0.16	4304 ± 58
1,3-DEU	316	H	324 to 379	22	12.38 ± 0.10	5122 ± 34
	318	C	321 to 356	14	11.78 ± 0.26	4907 ± 90
	D20	D	330 to 371	16	11.85 ± 0.26	4911 ± 84
	D19	D	326 to 371	24	12.52 ± 0.20	5152 ± 66

Several experiments using different cells were carried out for each urea derivative; the results are summarized in table 2 and figure 3. The few vapour pressures measured beyond the melting temperatures are not taken into account. The following vapour-pressure equations were chosen:

$$\text{MMU, } \lg(p/\text{kPa}) = 10.72 - 4562(K/T), \quad (2)$$

$$\text{MEU, } \lg(p/\text{kPa}) = 10.20 - 4496(K/T), \quad (3)$$

$$\text{MPU, } \lg(p/\text{kPa}) = 10.83 - 4608(K/T), \quad (4)$$

$$1,1\text{-DMU, } \lg(p/\text{kPa}) = 11.13 - 4655(K/T), \quad (5)$$

$$1,3\text{-DMU, } \lg(p/\text{kPa}) = 10.78 - 4454(K/T), \quad (6)$$

$$1,3\text{-DEU, } \lg(p/\text{kPa}) = 12.20 - 5047(K/T), \quad (7)$$

and the errors associated with their slopes (± 100) and intercepts (± 0.18) were estimated in the same way as for urea.

4. Discussion

A second-law treatment of each vapour-pressure equation gives the sublimation enthalpy and entropy changes of urea and its derivatives shown in table 3. The

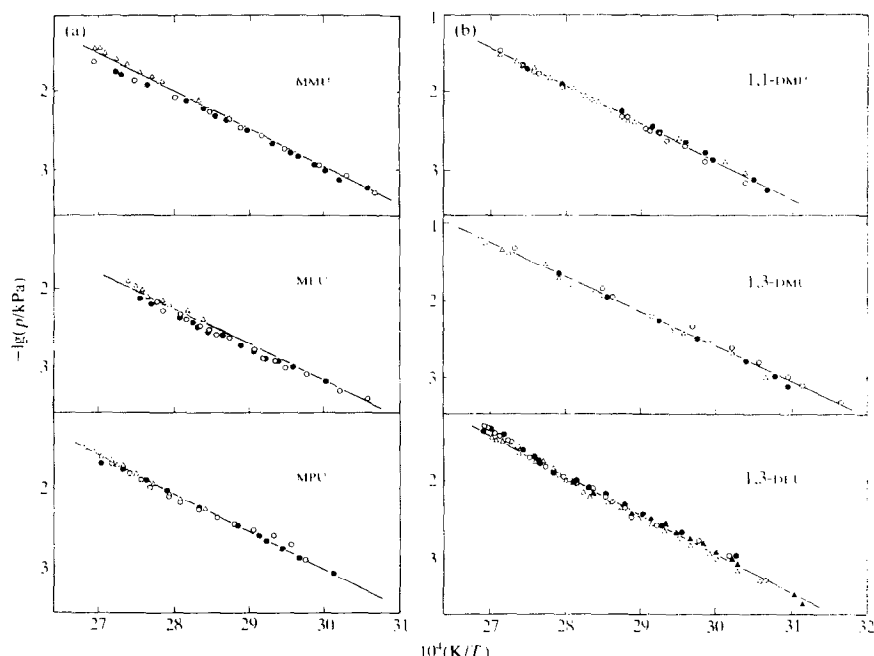


FIGURE 3. Experimental vapour pressure of (a), MMU: ●, Run 328; ○, Run 330; △, Run D26; MEU: ●, Run 323; ○, Run 327; △, Run D28; MPU: ●, Run 606; ○, Run 611; △, Run D29; and (b), 1,1-DMU: ●, Run 829; ○, Run 903; △, Run D11; 1,3-DMU: ●, Run 821; ○, Run 820; △, Run D06; 1,3-DEU: △, Run 313; ▲, Run 318; ○, Run D19; ●, Run D20.

standard sublimation enthalpy of urea was calculated by the third-law treatment of each experimental vapour pressure using the relation:

$$\Delta_{\text{sub}} H_m^\circ(T') = -RT \ln(p/p^\circ) + T\Delta_{\text{sub}} \Phi_m^\circ(T, T'), \quad (8)$$

where $T' = 298.15$ K, $p^\circ = 101.325$ kPa, and $\Phi_m^\circ(T, T') = -\Delta_f^\circ H_m^\circ/T + \Delta_0^\circ S_m^\circ$. Values of $\Phi_m^\circ(T, T')$ for the solid phase were calculated from the standard entropy, (104.5 ± 0.2) J · K⁻¹ · mol⁻¹ at T' , and the experimental enthalpies measured by Ruehrwein and Huffman;⁽²²⁾ those of the gaseous phase have been calculated by

TABLE 3. Molar sublimation enthalpies and entropy change of urea and its derivatives; errors are estimated (see text)

Compound	$\langle T \rangle / \text{K}$	$\Delta_{\text{sub}} H_m^\circ(\langle T \rangle) / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{sub}} S_m^\circ(\langle T \rangle) / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
urea	381	90.9 ± 1.9	159.0 ± 5.7
MMU	348	87.3 ± 1.9	167.0 ± 3.4
MEU	346	86.0 ± 1.9	156.0 ± 3.4
MPU	351	88.2 ± 1.9	169.0 ± 3.4
1,1-DMU	347	89.1 ± 1.9	174.7 ± 3.4
1,3-DMU	344	85.2 ± 1.9	168.0 ± 3.4
1,3-DEU	346	96.6 ± 1.9	195.2 ± 3.4

TABLE 4. Vapour pressure and third-law standard molar enthalpy of sublimation of urea at $T^* = 298.15$ K

$\frac{T}{K}$	$\frac{180\alpha}{\pi}$	$-\lg\left(\frac{p}{\text{kPa}}\right)$	$\frac{\Delta_{\text{sub}}H_m^{\circ}(T^*)}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{180\alpha}{\pi}$	$-\lg\left(\frac{p}{\text{kPa}}\right)$	$\frac{\Delta_{\text{sub}}H_m^{\circ}(T^*)}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{180\alpha}{\pi}$	$-\lg\left(\frac{p}{\text{kPa}}\right)$	$\frac{\Delta_{\text{sub}}H_m^{\circ}(T^*)}{\text{kJ}\cdot\text{mol}^{-1}}$
Run D08											
372	6	2.48	93.05	386	18	2.00	92.97	397	45	1.61	92.67
376	8	2.36	93.13	387	20	1.98	93.09	398	51	1.55	92.46
377	10	2.26	92.67	388	22	1.94	93.01	400	55	1.52	92.67
379	11	2.22	92.88	389	24	1.88	92.42	402	59	1.49	92.92
380	12	2.18	92.84	392	26	1.84	93.22	403	62	1.47	93.01
383	13	2.15	93.34	394	32	1.75	93.01	404	67	1.43	92.92
384	15	2.08	93.09	395	37	1.69	92.80	average: 92.88 ± 0.21			
385	17	2.03	92.97	396	42	1.64	92.67				
Run 626											
354	4	2.81	90.75	365	9	2.42	90.87	379	24	1.98	91.29
357	5	2.68	90.67	368	10	2.47	91.25	383	31	1.88	91.38
362	6	2.58	91.21	370	12	2.27	91.04	385	37	1.80	91.25
363	7	2.50	90.79	374	16	2.17	91.29	average: 91.00 ± 0.29			
Run D01											
365	3	2.78	93.38	383	12	2.18	93.59	399	40	1.66	93.51
368	4	2.66	93.30	386	14	2.11	93.80	402	50	1.56	93.47
371	6	2.48	92.80	387	17	2.03	93.47	403	56	1.51	93.30
377	8	2.36	93.43	389	20	1.96	93.43	405	68	1.43	93.13
379	9	2.31	93.55	395	28	1.81	93.72	average: 93.43 ± 0.25			
Run D02											
368	3	2.78	94.14	386	13	2.15	94.10	399	34	1.73	94.05
370	4	2.66	93.76	387	14	2.11	94.05	400	42	1.64	93.59
372	5	2.56	93.59	389	16	2.06	94.14	403	43	1.63	94.22
375	6	2.48	93.76	391	19	1.98	94.05	407	57	1.50	94.14
380	8	2.36	94.14	393	21	1.94	94.22	409	64	1.45	94.22
382	9	2.31	94.30	394	22	1.92	94.30	average: 94.05 ± 0.21			
383	10	2.26	94.18	396	25	1.86	94.35				
Run 821											
363	9	2.62	91.75	382	36	2.01	92.09	392	72	1.73	92.42
368	13	2.46	91.88	384	42	1.95	92.13	395	86	1.63	92.34
370	15	2.39	91.88	385	46	1.91	92.09	397	120	1.49	91.75
373	21	2.25	91.63	387	58	1.81	91.84	400	109	1.53	92.76
375	23	2.21	91.84	388	52	1.75	92.34	401	140	1.42	92.13
377	26	2.16	91.96	389	68	1.74	91.75	average: 92.05 ± 0.29			
380	31	2.04	92.13	391	64	1.76	92.38				
Run D04											
381	9	2.30	93.97	393	20	1.96	94.39	400	41	1.65	93.68
382	10	2.26	93.93	394	22	1.92	94.30	402	47	1.59	93.68
384	11	2.22	94.14	395	25	1.86	94.10	405	50	1.56	94.14
385	14	2.11	93.55	397	30	1.78	93.97	average: 94.01 ± 0.25			
388	16	2.06	93.93	398	33	1.74	93.89				
392	19	1.98	94.26	399	36	1.70	93.84				

Antonov⁽²³⁾ by the conventional statistical-thermodynamic method. The changes in $\Phi_m^\circ(T, T')$ for the sublimation of urea in our temperature range were practically constant at $164 \text{ kJ} \cdot \text{mol}^{-1}$. The third-law standard sublimation enthalpies calculated at each temperature are reported in table 4. The value $\Delta_{\text{sub}}H_m^\circ(T') = (93.0 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ is the weighted mean of the average values for the runs and the associated error is the standard deviation of those values. The final value is in close agreement with the $(94.3 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$ derived from the slope of equation (1), corrected to T' by using the enthalpy increments reported in the literature.^(22, 23) A value of $93.5 \text{ kJ} \cdot \text{mol}^{-1}$ was therefore chosen as the standard sublimation enthalpy change of the urea.

The agreement between second- and third-law results and the absence of trends in the calculated $\Delta_{\text{sub}}H_m^\circ(T')$ values suggested that uncertainties associated with the experimental measurements and calibration factors are of minor importance, so we believe that the overall error should not exceed $2 \text{ kJ} \cdot \text{mol}^{-1}$. Table 5 compares our selected $p(T)$ equation and sublimation enthalpy values with those in the literature; it shows that they lie between those of Suzuki *et al.*⁽¹⁴⁾ and Ritter Sutter,⁽¹⁵⁾ and the more recent observations of Trimble and Voorhoeve⁽¹⁶⁾ and de Wit *et al.*⁽¹⁷⁾

As concerns the urea derivatives, it is interesting to note that their vapour pressures are similar to those found for pure urea so that their sublimation enthalpies and entropies, except for those of 1,3-DEU, are comparable within the experimental uncertainties (see table 3).

Several opposing effects probably prevent the emergence of a unique trend from the present set of compounds. One can expect a decrease of the sublimation enthalpies in passing from urea (which shows the maximum number of intermolecular H-bonds in the solid state) to its alkyl derivatives. The lengthening of the alkyl chains promotes an absolute increase in $\Delta_{\text{vap}}H_m^\circ$ due to the increase of molar mass, but at the same time can induce changes in the intensities of the dipolar and dispersion interactions and variations in the geometric parameters of the elementary cell. In general the perturbation of the crystal field, relative to urea, is

TABLE 5. Vapour pressure and molar enthalpy of sublimation for urea ($T' = 298.15 \text{ K}$)

Reference	Method	$\langle T \rangle / \text{K}$	N	A	B	$\Delta_{\text{sub}}H_m^\circ(T)$	$\Delta_{\text{sub}}H_m^\circ(T')$	$\Delta_{\text{sub}}H_m^\circ(T')$
						$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
						second-law		third-law
14	Knudsen	357	8	9.5	4579	87.6 ± 0.9	90 ± 0.9	
15	Knudsen	300				88.2^a	88.2	
16	Calorimetry	360	10	10.5^c	4930	94.4	96.9^b	
17	Torsion- Knudsen	351		11.04^d	5079	96.9	98.6	
This work	Torsion	381	99	10.30 ± 0.30	4570 ± 100	90.9 ± 1.9	94.3 ± 1.9	93.0 ± 1.3

^a As reported in reference 17.

^b Corrected to T' with the enthalpy increments reported in references 22 and 23.

^c Calculated from the experimental points drawn in figure of reference 16 since no $p(T)$ equation is reported in the text.

^d Calculated from mean values reported in the work.

TABLE 6. Thermodynamic quantities for urea derivatives

Compound	p ^a kPa	$\Delta_{fus}H_m^\circ$ ^b kJ·mol ⁻¹	$\Delta_{vap}H_m^\circ$ kJ·mol ⁻¹	T_{fus} K	T_{vap} K	
					this work	literature
MMU	3.3×10^{-2}	15.9 ± 0.1	71.4 ± 2.0	373.8 ± 0.1	574	Decomposes
MEU	9.3×10^{-3}	14.9 ± 0.1	72.0 ± 2.1	367.7 ± 0.1	606	Decomposes
MPU	5.4×10^{-2}	14.7 ± 0.2	73.5 ± 2.1	380.9 ± 0.1	563	?
1,1-DMU	6.8	29.6 ± 0.1	59.5 ± 2.0	454.2 ± 0.1	548	?
1,3-DMU	1.1×10^{-1}	13.6 ± 0.2	71.6 ± 2.1	379.4 ± 0.2	542	541
1,3-DEU	1.1×10^{-1}	12.5 ± 0.2^c	84.1 ± 2.5	383.5 ± 0.2	517	536

^a Vapour pressure at the melting temperature.^b Measured calorimetrically.⁽²⁴⁾^c Taking into account the enthalpy of an α -to- β phase transition: $\Delta_{trs}H_m^\circ = (1.9 \pm 0.1)$ kJ·mol⁻¹ at 340 K as found by Della Gatta *et al.*⁽²⁴⁾

not easy to predict. The entropy in turn can also undergo the odd-pair effect due to the number of carbon atoms in the alkyl chain.

Recently some of us⁽²⁴⁾ have measured calorimetrically the enthalpies of melting of these compounds, and the results obtained are summarized in table 6. An estimate can be made of the boiling temperatures of these compounds from their vapour pressures combined with the enthalpies of melting and assuming the enthalpies of the condensed and gaseous phases to be equal. Unfortunately, most of these compounds decompose before boiling except 1,3-DMU and 1,3-DEU. The comparison between the experimental boiling temperatures of these compounds⁽²⁵⁾ and our estimated values shows (see table 6) good agreement in view of the large uncertainties associated with our procedure.

NOTE ADDED IN PROOF

Recently Kasulin and Kozyro⁽²⁶⁾ have determined a new set of $\Delta_{sub}H_m^\circ(T)$ values for urea and its derivatives: MMU, MEU, 1,1-DMU, and 1,3-DEU equal to 99.3, 100.3, 99.1, and 95.6 kJ·mol⁻¹, respectively. These values, obtained from vapour-pressure measurements carried out by the Knudsen method, seem to be higher than those reported in this work. In view of the different techniques and in the absence of the number of the experimental points and the uncertainties associated with their method, at present it is difficult to make a constructive comment.

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