J. Chem. Eng. Data **2006,** *51,* 79−87

Measurement and Prediction of Thermochemical Properties: Improved Increments for the Estimation of Enthalpies of Sublimation and Standard Enthalpies of Formation of Alkyl Derivatives of Urea

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This work has been undertaken in order to obtain data on vapor pressures of alkyl derivatives of urea and to revise the group additivity values necessary for predicting their sublimation enthalpies and standard enthalpies of formation at the reference temperature $T = 298.15$ K. Molar enthalpies of sublimation of urea, 1-methylurea, 1-*n*-propylurea, 1-*n*-butylurea, 1-*sec*-butylurea, 1-*tert*-butylurea, 1,1-dimethylurea, 1,1-diethylurea, 1,3-dimethylurea, and 1,3-diethylurea were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. Thermochemical investigations of 16 alkyl derivatives of urea available in the literature were collected and combined with our own experimental results to obtain their reliable standard molar enthalpies of formation at $T = 298.15$ K in the condensed or in the gaseous state. Ab initio calculations of alkyl derivatives of urea have been performed using G3(MP2), and results from the homodesmic reactions are in acceptable agreement with experiment. New results help to resolve uncertainties in the available thermochemical data on homologues of the alkylureas studied.

Introduction

One of the long-term aims of the work in our laboratories has been to build a framework of experimental data from which one may use to study the relation between energy content and molecular structure and to calculate values for the enthalpies of formation of many hundreds of compounds without need of further experimental measurements. Among the important groups of compounds for which suitable experimental data are needed for a basic framework of this kind are alkyl derivatives of carbamide (or urea). The thermochemical data on alkylureas is sparse and often problematic, especially for the sublimation enthalpies. Even for urea itself, the spread of the available data on sublimation enthalpies is >20 kJ·mol^{-1} (see Table 1). Generally, there are two, very disparate, data sets for the enthalpies of sublimation of alkylureas that are reported in the literature. The first set was measured[1−9] at the Belorussian State University (Minsk, Belarus) using both the Knudsen technique and vaporization calorimetry. The second data set was measured[10−12] at the University of Rome ("La Sapienza"), Italy, using a torsion-effusion technique. A significant difference in vapor pressures of diverse alkylureas has been observed (see Supporting Information) between results measured in these laboratories. The corresponding sublimations enthalpies are in disagreement randomly, by about (5 to 12) kJ·mol^{-1} (Table 1). In the meantime, some new improvements in the data treatment of the experiments with the Knudsen cell have been suggested.[13] These have been applied as a correction to the previous results on the vapor pressures of alkylureas measured by the Minsk laboratory.[2] However, after these corrections, the discrepancies between two aforementioned data sets on sublimation enthalpies still remain. Thus, it remains a question as to which data set is correct and should be recommended for further thermochemical calculations? A reasonable way to resolve this contradiction would be additional measurements using another experimental technique.

One of the most suitable methods for investigation of vapor pressures of alkylureas is the transpiration method, which is well-established in the thermochemical laboratory in Rostock.[13−15] This method offers three advantages. The first advantage is the opportunity to remove occluded moisture in preliminary experiments by flashing the sample with dry nitrogen, and a constant vapor pressure would indicate that all moisture had been removed. The second arises from being able to measure the vapor pressures near ambient temperature, especially for labile materials, where it is essential to minimize thermal stress. The third is the protection against oxidation and decomposition of the sample provided by the inert nitrogen especially at higher temperatures. For these reasons, we decided to determine the thermochemical quantities of alkylureas by the transpiration method. We tested our experimental and calculation procedures with measurements on urea, for which temperature dependence of the vapor pressure is reliable.[7,16,17] The derived new values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$ of 1-methylurea, 1-*n*-propylurea, 1-*n*-

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10.1021/je050230z CCC: $33.50

Table 1. Compilation of Data on Enthalpies of Sublimation $\Delta_{cr}^{g}H_m$(298.15 K) of Alkylureas

compounds	technique[a]	temperature range K	$\Delta_{cr}^{g}H_m$ (T_{av}) kJ·mol^{-1}	$\Delta_{cr}^{g}C_p$[b] J·mol^{-1}·K^{-1}	$\Delta_{cr}^{g}H_m$(298.15K)[c] kJ·mol^{-1}	ref
urea	K	346.0−368.2	87.5 ± 1.2	−27.0	89.0 ± 1.2	18
	TE	337.2−361.3	96.9		98.3	17
	TE	354−409	74.6 ± 3.4		76.9 ± 3.4	11
	K	329.1−403.1	94.6 ± 1.0		96.3 ± 1.0	2, 13
	C	350	94.6 ± 0.5		96.0 ± 0.5.	2, 13
	T	358.3−402.0	93.3 ± 0.3		95.5 ± 0.3	this work
1-methylurea	TE	326−371	87.3 ± 1.9	−39.0	89.3 ± 1.9	11
	TE	339−372	93.2 ± 1.1		95.4 ± 1.1	10
	C	350	94.4 ± 0.4		96.4 ± 0.4	2, 13
	K	322.8−371.5	96.9 ± 1.2		98.8 ± 1.2	2, 13
	T	331.1−365.7	93.5 ± **0.5**		95.5 ± **0.5**	this work
1-ethylurea	TE	327−365	86.0 ± 1.9	−48.0	88.3 ± 1.9	11
	TE	341−368	91.8 ± 1.2		94.5 ± 1.2	10
	C	350	96.4 ± 1.1		98.9 ± 1.1	2, 13
	K	323.3−364.1	98.1 ± 1.1		100.2 ± 1.1	2, 13
1-*n*-propylurea	TE	332−373	88.2 ± 1.9	−58.1	91.3 ± 1.9	11
	TE	346−386	90.7 ± 1.1		94.7 ± 1.1	10
	T	333.2−369.5	98.3 ± **0.6**		101.4 ± **0.6**	this work
1-isopropylurea	TE	368−411	100.6 ± 1.3[d]	−19.7	102.4 ± 1.3[d]	10
	C	350	97.2 ± 0.6		98.0 ± 0.6	2, 13
	K	333.2−372.1	96.7 ± 1.6		97.8 ± 1.6	2, 13
1-*n*-butylurea	TE	346−369	99.0 ± 4.0	−66.3	103.0 ± 4.0	12
	C	350	101.1 ± 0.4		104.5 ± 0.4	2, 13
	K	345.2−368.1	100.7 ± 2.4[e]		104.6 ± 2.4	2, 13
	T	346.2−367.1	101.9 ± **0.7**		105.8 ± **0.7**	this work
1-isobutylurea	TE	353−402	101.1 ± 1.1	−31.9	103.6 ± 1.1	10
1-*sec*-butylurea	C	350	102.4 ± 0.5	−33.4	104.1 ± 0.5	2, 13
	K	338.2−372.2	104.3 ± 0.8		106.2 ± 0.8	2, 13
	T	344.9−393.6	99.6 ± 0.5		101.9 ± 0.5	this work
1-*tert*-butylurea	TE	359−399	101.6 ± 0.7	−22.6	103.4 ± 0.7	10
	C	350	94.4 ± 0.9		95.6 ± 0.9	2, 13
	K	333.2−372.2	97.6 ± 0.8		98.8 ± 0.8	2, 13
	T	335.3−397.2	96.7 ± 0.4		98.2 ± 0.4	this work
1,1-dimethylurea	TE	326−369	89.1 ± 1.9	−27.1	90.4 ± 1.9	11
	TE	342−372	92.5 ± 1.3		94.1 ± 1.3	10
	C	350	93.3 ± 0.5		94.7 ± 0.5	2, 13
	K	323.2−363.4	94.7 ± 1.4		96.1 ± 1.4	2, 13
	T	346.3−398.3	92.0 ± 0.3		93.5 ± 0.3	this work
1,1-diethylurea	C	350	94.7 ± 0.2	−24.1	96.0 ± 0.2	2, 13
	K	305.1−347.1	95.5 ± 0.8		96.2 ± 0.8	2, 13
	T	312.2−339.0	95.1 ± **0.7**		95.7 ± **0.7**	this work
1,3-dimethylurea	TE	316−373	85.2 ± 1.9	−34.4	86.8 ± 1.9	11
	TE	334−373	87.2 ± 0.6		89.1 ± 0.6	10
	C	350	86.6 ± 0.5		88.4 ± 0.5	2, 13
	K	317.1−377.6	87.6 ± 1.0		90.1 ± 1.0	2, 13
	T	313.1−357.6	88.0 ± **0.4**		89.3 ± **0.4**	this work
1,3-diethylurea	TE	321−371	96.6 ± 1.9	−58.2	99.4 ± 1.9	11
	TE	345−378	96.8 ± 0.9		100.5 ± 0.9	10
	C	350	95.6 ± 0.6		98.6 ± 0.6	2, 13
	K	343.2−384.7	91.5 ± 1.4[f]		95.1 ± 1.4	2, 13
	T	343.2−379.2	91.7 ± 0.3		95.4 ± 0.3	this work
1,1-di-*tert*-butylurea	C	350	90.0 ± 1.0	−20.1	91.1 ± 1.0	2, 13
	K	323.3−372.3	91.9 ± 0.9		92.9 ± 0.7	2, 13

[a] Techniques: TE, torsion-effusion method; T, transpiration; C, calorimetry; K, Knudsen cell. [b] The molar heat capacity difference between the solid and the gaseous phases (see text). [c] Derived using eqs 2 and 3 with the molar heat capacity difference $\Delta_{cr}^{g}C_p$. [d] The value of $\Delta_{cr}^{g}H_m$ is overestimated because in the temperature range (368 to 411) K the phase transition occurs at $T_{tr} = 376$ K. Any corrections are impossible because of the absence of primary experimental data. [e] The orginal value of $\Delta_{cr}^{g}H_m$ was corrected because measurements around transition point at $T_{tr} = 345$ K should not be taken into account. [f] The orginal value of $\Delta_{cr}^{g}H_m$ was corrected because measurements around transition point at $T_{tr} = 340.8$ K should not be taken into account.

butylurea, 1-*sec*-butylurea, 1-*tert*-butylurea, 1,1-dimethylurea, 1,1-diethylurea, 1,3-dimethylurea, and 1,3-diethylurea are close to those measured in the Minsk laboratory earlier.[2] These values together with the values already available from the literature were used to revise the group-additive scheme for the prediction of the enthalpies of sublimation and enthalpies of formation of the alkyl derivatives of urea.

Experimental Section

Materials. Pure samples of 1-*sec*-butylurea, 1-*tert*-butylurea, 1,1-dimethylurea, 1,1-diethylurea, 1,3-dimethylurea, and 1,3-diethylurea were from the same batch as reported in the ref 3. Samples of urea, 1-methylurea, 1-*n*-propylurea, and 1-*n*-butylurea were of commercial origin (Alfa, Aldrich, and Fluka). Specimens were purified by repeated sublimation under reduced pressure shortly before the beginning of the measurements. The degree of purity was determined using a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 7.2 dm^3·h^{-1}. A capillary column HP-5 (stationary phase cross-linked 5 % PH ME silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The standard temperature program of the GC was $T = 323$ K for 60 s followed by heating to $T = 523$ K at the rate of 20 K·min^{-1}. No impurities (mass fraction greater than 0.02 %) could be detected in the samples used for the vapor pressure measurements.

Vapor pressures of alkylureas were determined using the transpiration method. The method has been described in detail before[14−16] and has been proven to give results in agreement with other established techniques. The enthalpies of sublimation ($\Delta_{cr}^{g}H_m$) of alkylureas were derived from the temperature dependence of the vapor pressures. A sample of approximately 0.5 g was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. Preheated nitrogen stream was passed through the U-tube at constant temperature (± 0.1 K). The flow rate of the nitrogen stream was measured using a soap film bubble flowmeter ± (0.2 to 0.3) % and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The apparatus was tested at different flow rates of the carrier gas in order to check the lower boundary of the flow, below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the one from the transpiration method. In our apparatus the contribution due to diffusion was negligible at flow rates down to 0.5 dm^3·h^{-1}. The upper limit for our apparatus was a flow rate of 12.5 dm^3·h^{-1}. Thus, experiments were carried out using flow rates ranging from (1.6 to 10) dm^3·h^{-1}, which ensured that the transporting gas was in saturated equilibrium with the coexisting solid phase in the saturation tube. The amount of material transported was condensed in a cooled trap at 243 K. The amount of condensed substance was determined by GC analysis using an external standard (*n*-decane, *n*-undecane, or *n*-dodecane).

The saturated vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a defined period of time. Assuming that Dalton's law of partial pressures when applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{\text{sat}} = m_i R T_a / V M_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i) \tag{1}$$

where $R = 8.314510$ J·K^{-1}·mol^{-1}; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of transporting gas, and T_a is the temperature of the soap film bubble flowmeter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements.

Ab Initio Calculations

Standard ab initio molecular orbital calculations were performed with the Gaussian 03 revision B.04 series of programs.[19] Energies were obtained at the G3(MP2) level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second rows of the periodic chart based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller−Plesset perturbation theory is G3(MP2) theory.[20,21] This method saves considerable computational time as compared to G3 theory with limited loss in accuracy but is much more accurate that G2(MP2) theory. G3(MP2) theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartree−Fock theory followed by a series of single-point energy calculations at the MP2(Full)/6-31G(d), QCISD(T)/6-31G(d), and MP2/GTMP2Large levels of theory (for details see ref 15).

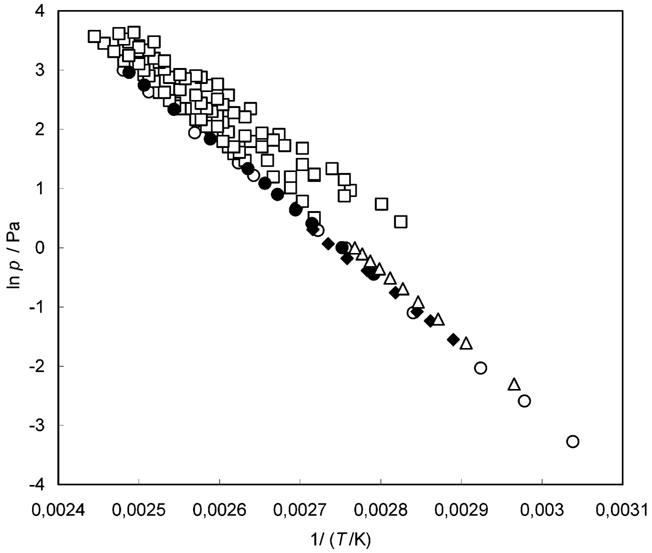


Figure 1. Experimental data of the vapor pressures of the urea. ●, this work; □, ref 11; ○, ref 13; △, ref 17; ▲, ref 18.

The enthalpy value of studied compounds at $T = 298$ K was evaluated according to standard thermodynamic procedures.[22]

Results and Discussion

Vapor Pressure Measurements. Experimental vapor pressures of alkylureas have been measured using the transpiration method over a broad (50 K) temperature range. In each case, the measurements have been performed as close as possible to the reference temperature of 298.15 K. The following equation[15,16]

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_{cr}^{g} C_p \ln\left(\frac{T}{T_0}\right) \tag{2}$$

was fitted to the experimental p,T data using a and b as adjustable parameters. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which in this case is 298.15 K). Consequently, from eq 2 the expression for the sublimation enthalpy at temperature T is

$$\Delta_{cr}^{g} H_m(T) = -b + \Delta_{cr}^{g} C_p T \tag{3}$$

Values of $\Delta_{cr}^{g}C_p$ have been derived earlier.[3] Experimental results and parameters a and b are listed in Table 2.

Enthalpies of Sublimation $\boldsymbol{\Delta_{cr}^{g}H_m}$**.** The collection of the available experimental results and derived $\Delta_{cr}^{g}H_m$(298.15 K) values for alkyl derivatives of ureas is presented in Table 1. Authors of these cited works[10−13,17,18] adjusted their measured values of $\Delta_{cr}^{g}H_m$ to the reference temperature, $T = 298.15$ K, by different and sometimes ill-defined methods. It is for this reason that in this work the original published experimental results were re-adjusted to the reference temperature $T = 298.15$ K in the same manner as our own results using eqs 2 and 3.

To establish the validity of the transpiration method for alkyl derivatives of urea, the admittedly reliable[7,17,18] enthalpy of sublimation of urea itself has been measured in this work. Our vapor pressures and enthalpy of sublimation $\Delta_{cr}^{g}H_m$ are in a very good agreement with those from the literature[7,17,18] (see Table 1).

As shown in the Figure 1, the vapor pressure of urea measured by different experimental techniques (except for data by Ferro et al.[11]) are in acceptable agreement. The corresponding values of $\Delta_{cr}^{g}H_m$ of urea, which were indirectly derived from these results, are also in agreement. They are also in agreement with

Table 2. Vapor Pressures p and $\Delta_{cr}^{g}H_m$ Obtained by the Transpiration Method[a]

T	m	$V(N_2)$	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_m$	T	m	$V(N_2)$	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_m$
K[b]	mg[c]	dm^3	Pa[d]	Pa	kJ·mol^{-1}	K[b]	mg[c]	dm^3	Pa[d]	Pa	kJ·mol^{-1}
Urea[e]; $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (95.52 \pm 0.30)\ \mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{290.4}{R} - \frac{103571.4}{R(T/\mathrm{K})} - \frac{27.0}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
358.3	3.1	196.89	0.64	0.00	93.90	379.5	4.2	44.86	3.80	0.09	93.33
363.4	3.9	158.13	1.00	0.00	93.76	386.3	3.0	19.51	6.27	0.01	93.14
368.4	6.5	175.31	1.51	−0.01	93.63	393.2	10.1	39.59	10.36	−0.03	92.96
371.2	6.5	140.56	1.89	−0.02	93.55	399.0	9.6	24.99	15.59	−0.11	92.80
374.3	10.8	178.50	2.46	0.00	93.47	402.0	9.9	20.81	19.31	−0.03	92.72
376.5	8.0	109.63	2.96	0.03	93.41						
1-Methylurea; $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (95.48 \pm 0.45)\ \mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{318.2}{R} - \frac{107110.1}{R(T/\mathrm{K})} - \frac{39.0}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
333.1	0.98	80.55	0.40	0.01	94.12	356.2	1.04	9.69	3.56	0.02	93.22
338.1	1.29	67.09	0.64	−0.01	93.93	359.6	1.09	7.65	4.74	−0.03	93.09
342.7	0.92	30.28	1.00	−0.02	93.75	362.7	1.03	5.61	6.12	−0.13	92.96
346.1	0.90	21.41	1.40	−0.01	93.61	365.7	0.94	3.87	8.03	−0.01	92.85
349.2	0.92	16.01	1.92	0.04	93.49	365.7	1.05	4.28	8.15	0.11	92.85
352.2	0.98	12.95	2.52	0.03	93.37						
1-Propylurea; $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (101.36 \pm 0.57)\ \mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{348.9}{R} - \frac{118677.8}{R(T/\mathrm{K})} - \frac{58.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
333.2	0.56	72.70	0.19	0.00	99.32	349.2	0.69	16.78	0.99	0.01	98.39
337.4	0.83	66.24	0.30	0.00	99.08	350.2	0.37	8.17	1.08	0.00	98.33
342.2	0.49	24.97	0.47	−0.02	98.80	354.1	0.68	10.32	1.58	0.01	98.11
345.7	0.36	12.20	0.72	0.02	98.60	355.2	0.31	4.21	1.76	0.02	98.04
346.1	0.62	20.25	0.74	0.01	98.57	357.3	0.78	8.68	2.17	0.06	97.92
348.7	0.29	7.48	0.94	0.00	98.42						
1-*n*-Butylurea; $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (105.82 \pm 0.70)\ \mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{365.6}{R} - \frac{125585.1}{R(T/\mathrm{K})} - \frac{66.3}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
346.3	0.33	16.16	0.43	0.00	102.63	359.9	0.24	2.98	1.69	0.04	101.73
349.5	0.33	11.92	0.59	−0.01	102.41	363.0	0.31	2.98	2.21	−0.01	101.52
352.5	0.36	9.44	0.81	0.01	102.22	363.1	0.34	3.28	2.20	−0.02	101.51
352.5	0.33	8.74	0.80	0.00	102.22	364.9	0.33	2.70	2.57	−0.05	101.40
356.5	0.36	6.46	1.20	0.00	101.95	367.2	0.34	2.20	3.27	0.04	101.24
1-*sec*-Butylurea; $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (101.94 \pm 0.54)\ \mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{318.3}{R} - \frac{111901.0}{R(T/\mathrm{K})} - \frac{33.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
344.9	0.64	50.87	0.26	0.00	100.38	370.9	2.82	19.18	3.11	0.07	99.51
348.2	1.25	69.69	0.38	0.01	100.27	373.1	2.24	12.94	3.66	−0.02	99.44
350.2	0.64	29.99	0.45	0.00	100.21	375.4	2.24	10.16	4.66	0.17	99.36
351.6	1.38	55.07	0.53	0.01	100.16	376.4	2.82	12.13	4.93	0.03	99.33
351.6	1.2	52.64	0.48	−0.04	100.16	379.9	2.87	9.32	6.53	−0.02	99.21
356.4	2.26	58.73	0.81	−0.01	100.00	381.7	2.15	5.88	7.76	0.18	99.15
359.0	3.09	61.68	1.06	0.02	99.91	383.2	2.68	6.70	8.47	−0.08	99.10
360.6	1.44	26.39	1.15	−0.05	99.86	385.4	2.36	4.79	10.43	0.17	99.03
361.9	3.32	49.32	1.43	0.07	99.82	387.0	2.69	4.98	11.46	−0.15	98.98
363.2	1.45	19.84	1.55	0.01	99.77	390.8	2.92	4.07	15.22	−0.44	98.85
366.6	2.41	23.76	2.15	0.06	99.66	393.6	2.92	3.17	19.56	0.05	98.75
369.7	1.86	15.50	2.54	−0.21	99.55						
1-*tert*-Butylurea; $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (98.21 \pm 0.43)\ \mathrm{kJ \cdot mol^{-1}}$ $\ln(p/\mathrm{Pa}) = \frac{305.2}{R} - \frac{104948.0}{R(T/\mathrm{K})} - \frac{22.6}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
335.3	0.58	45.21	0.27	−0.01	97.37	376.1	1.06	1.88	11.88	−0.53	96.45
340.3	0.83	34.75	0.51	0.03	97.26	379.2	1.16	1.51	16.35	0.45	96.38
348.2	0.76	15.40	1.04	0.01	97.08	382.2	1.29	1.36	20.20	−0.02	96.31
357.0	0.88	7.91	2.35	−0.02	96.88	385.2	1.07	0.91	25.02	−0.57	96.24
360.2	0.99	6.63	3.15	−0.01	96.81	388.2	1.20	0.79	32.20	−0.08	96.18
363.1	1.04	5.27	4.19	0.08	96.74	391.2	1.31	0.67	41.48	0.91	96.11
366.0	1.07	4.34	5.23	−0.04	96.68	394.2	1.49	0.63	50.11	−0.68	96.04
369.1	1.10	3.32	7.02	0.14	96.61	397.2	1.80	0.59	64.41	1.04	95.97
372.2	1.09	2.64	8.74	−0.20	96.54						

Table 2 (Continued)

T	m	$V(N_2)$	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_m$	T	m	$V(N_2)$	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_m$
K[b]	mg[c]	dm^3	Pa[d]	Pa	kJ·mol^{-1}	K[b]	mg[c]	dm^3	Pa[d]	Pa	kJ·mol^{-1}
1,1-Dimethylurea; $\Delta_{cr}^{g}H_m(298.15\ K) = (93.48 \pm 0.34)$ kJ·mol^{-1} $\ln(p/Pa) = \frac{306.9}{R} - \frac{101564.8}{R(T/K)} - \frac{27.1}{R}\ln\left(\frac{T/K}{298.15}\right)$											
346.3	1.87	16.75	3.14	−0.01	92.18	380.2	2.04	1.06	54.27	0.32	91.26
356.1	1.73	6.47	7.53	−0.06	91.92	383.3	3.44	1.43	67.39	−0.74	91.18
362.2	2.03	4.55	12.56	−0.23	91.75	386.3	2.25	0.73	86.51	1.43	91.10
365.2	2.14	3.63	16.62	0.19	91.67	389.3	2.65	0.70	105.95	0.09	91.02
368.1	2.04	2.79	20.55	−0.29	91.59	392.2	2.75	0.60	130.09	−0.23	90.94
371.2	2.58	2.65	27.35	0.59	91.51	395.2	2.76	0.49	159.23	−2.37	90.85
374.2	2.45	2.00	34.44	0.50	91.43	398.3	2.85	0.41	197.68	−2.02	90.77
377.2	2.33	1.52	43.28	0.41	91.34						
1,1-Diethylurea; $\Delta_{cr}^{g}H_m(298.15\ K) = (95.74 \pm 0.69)$ kJ·mol^{-1} $\ln(p/Pa) = \frac{326.7}{R} - \frac{102929.3}{R(T/K)} - \frac{24.1}{R}\ln\left(\frac{T/K}{298.15}\right)$											
312.2	2.25	77.14	0.62	0.01	95.41	326.2	1.96	14.23	2.90	−0.04	95.07
313.1	1.69	52.67	0.68	0.01	95.38	328.2	1.61	9.64	3.53	−0.11	95.02
315.2	2.97	71.63	0.88	0.01	95.33	329.2	2.11	11.48	3.89	−0.16	95.00
316.7	2.51	50.43	1.06	0.03	95.30	330.2	2.27	10.65	4.53	0.03	94.97
320.1	1.83	25.99	1.50	−0.01	95.22	333.0	2.03	7.07	6.10	0.08	94.91
320.2	1.57	22.04	1.50	−0.02	95.21	336.7	2.65	6.30	8.94	0.17	94.82
324.2	2.11	19.56	2.28	−0.09	95.12	339.1	2.28	4.20	11.54	0.40	94.76
1,3-Dimethylurea; $\Delta_{cr}^{g}H_m(298.15\ K) = (89.31 \pm 0.39)$kJ·mol^{-1} $\ln(p/Pa) = \frac{305.7}{R} - \frac{99569.4}{R(T/K)} - \frac{34.4}{R}\ln\left(\frac{T/K}{298.15}\right)$											
313.3	0.76	110.69	0.19	0.00	88.79	343.2	0.79	6.03	3.68	0.02	87.76
322.9	1.14	62.30	0.51	−0.01	88.46	347.3	0.71	3.71	5.32	0.07	87.62
326.9	0.77	27.81	0.77	−0.01	88.33	351.4	0.73	2.78	7.38	−0.07	87.48
330.9	0.67	15.76	1.19	0.03	88.19	354.6	0.83	2.41	9.66	−0.10	87.37
335.0	0.67	10.66	1.75	0.04	88.05	357.7	0.89	1.95	12.73	0.11	87.27
339.0	1.04	12.05	2.42	−0.07	87.91						
1,3-Diethylurea; $\Delta_{cr}^{g}H_m(298.15\ K) = (95.38 \pm 0.27)$ kJ·mol^{-1} $\ln(p/Pa) = \frac{342.6}{R} - \frac{112736.6}{R(T/K)} - \frac{58.2}{R}\ln\left(\frac{T/K}{298.15}\right)$											
343.1	0.89	9.27	2.05	0.02	92.77	364.2	1.19	1.91	13.22	0.08	91.54
346.2	0.87	6.83	2.70	−0.01	92.59	365.7	1.24	1.79	14.74	−0.13	91.46
349.2	0.98	5.92	3.53	−0.03	92.42	367.2	1.20	1.54	16.52	−0.29	91.37
352.3	1.27	5.69	4.76	0.05	92.24	370.1	1.22	1.24	21.08	−0.26	91.20
355.2	1.47	5.06	6.17	0.05	92.06	373.2	2.34	1.79	27.76	0.59	91.02
358.2	1.52	4.14	7.83	−0.11	91.89	374.6	2.46	1.73	30.23	−0.10	90.94
359.6	1.16	2.78	8.85	−0.07	91.81	376.2	2.31	1.42	34.61	0.15	90.84
361.2	1.22	2.53	10.28	0.06	91.72	379.2	2.40	1.17	43.48	0.29	90.67

[a] m is mass of transferred sample. $V(N_2)$ is the volume of nitrogen used to transfer mass m of sample. p is vapor pressure. [b] Temperature of saturation. N_2 gas flow (1.6 to 6.1) dm^3·h^{-1}. [c] Mass of transferred sample condensed at $T = 243$ K. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at $T = 243$ K. [e] Mass of transferred sample was condensed at $T = 293$ K and was weighted with the accuracy ± 0.0001 g.

the value of (96.3 ± 1.0) kJ·mol^{-1} measured directly by calorimetry.[2] It is significant that an enormous spread of the experimental vapor pressures of urea was specific for measurements by Ferro et al.[11] using the torsion-effusion method. The spread is hardly explainable due to peculiarities of the experimental technique, and also no comments could be found in the original work.[11] The purification and attestatation of the samples for measurements by Ferro et al.[11] seems to be sufficient. Unfortunately, the primary data for vapor pressure measurements are reported only in the case of urea; for other alkylureas measured in the Rome laboratory, only approximations of the experimental data have been published.[10,11] However, those authors reasserted:[10] "Critical analysis of the error sources associated with the torsion-effusion method (instrument constants, temperature measurements, torsion angle determinations, thermodynamic equilibrium conditions in the effusion cell, etc.) suggests that the intercepts of the pressure−temperature equations may be affected by some uncertainties, those associated with slope being decidedly minor." Despite such an optimistic assertion, the disagreements of about (5 to 12) kJ·mol^{-1} with another set of available data, and even with own earlier results, are hardly explainable. It should be noted that most of the alkylureas (see Supporting Information) were measured in the Rome laboratory twice.[10,11] Surprisingly, the data for 1-ethylurea, 1-butylurea, and 1,3-diethylurea were reproduced, but for 1-methylurea, 1-propylurea, and 1,3-dimethylurea the disagreement between two experimental runs was dramatic. Again, no reasonable explanation for these artifacts could be found in the original works.[10,11] In contrast, the agreement of the $\Delta_{cr}^{g}H_m$ results on alkylureas derived from Knudsen experiments[2] and those from the transpiration method (this work) are in a close agreement (see Table 1). The direct calorimetric results measured in the Minsk laboratory[2] confirm the sublimation enthal-

Table 3. Selection of Experimental Data on Thermochemical Properties of Alkylureas at 298.15 K

compound	$\Delta_{cr}^{g}H_m$(298K) kJ·mol^{-1}	$\Delta_f H_m^\circ$(cr)[e] kJ·mol^{-1}	$\Delta_f H_m^\circ$(g) kJ·mol^{-1}
urea	96.0 ± 0.5[a]	−333.6 ± 0.6	−237.6 ± 0.8
1-methylurea	95.9 ± 0.5[a]	−327.8 ± 1.4[i]	−231.9 ± 1.5
1-ethylurea	99.3 ± 0.8[b]	−357.8 ± 0.7	−258.5 ± 1.1
1-*n*-propylurea	101.4 ± 0.6[c]		
1-isopropylurea	98.1 ± 0.6[b]	−389.5 ± 1.3	−291.4 ± 1.4
1-*n*-butylurea	106.7 ± 0.7[f]	−419.5 ± 3.3	−314.5 ± 3.4
1-isobutylurea	103.6 ± 1.1[d]		
1-*sec*-butylurea	101.9 ± 0.5[c]	−413.2 ± 1.5	−311.3 ± 1.6
1-*tert*-butylurea	97.8 ± 0.5[a]	−414.7 ± 0.9	−316.9 ± 1.0
1,1-dimethylurea	93.5 ± 0.3[c]	−319.1 ± 0.7	−224.2 ± 0.8
1,1-diethylurea	95.8 ± 0.5[a]	−372.2 ± 1.1	−276.4 ± 1.2
1,3-dimethylurea	88.8 ± 0.4[a]	−313.7 ± 1.2	−224.9 ± 1.3
1,3-diethylurea	97.1 ± 0.3[g]	−379.8 ± 1.8	−284.5 ± 1.8
1,1-di-*tert*-butylurea	93.6 ± 0.7[h]	−499.8 ± 4.2	−408.1 ± 4.3

[a] Average value from this work and those from ref 2. [b] Average derived in ref 2. [c] This work. [d] From ref 10. [e] Data from ref 1. [f] The sum of enthalpy of sublimation (105.8 ± 0.7) kJ·mol^{-1} derived in this work, and the enthalpy of phase transition 0.9 kJ·mol^{-1} at 345 K from ref 3. [g] The sum of enthalpy of sublimation (95.4 ± 0.3) kJ·mol^{-1} derived in this work, and the enthalpy of phase transition 1.7 kJ·mol^{-1} at 340.8 K from ref 3. [h] The sum of enthalpy of sublimation (91.7 ± 0.7) kJ·mol^{-1} derived in this work, and the enthalpy of phase transition 1.9 kJ·mol^{-1} at 301.7 K from ref 3. [i] Data from ref 28.

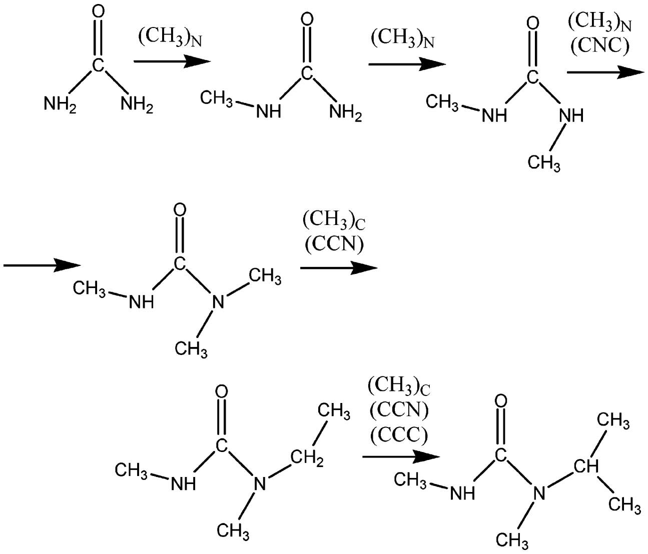
pies derived by the transpiration and the Knudsen method (see Table 1). Also close agreement of the vapor pressures of alkylureas measured by transpiration and Knudsen methods is demonstrated graphically in the Supporting Information. Since the values for the sublimation enthalpies of alkyl derivatives of urea measured independently in Minsk and in Rostock are consistent, values of the sublimation enthalpies of alkylureas have been averaged and have been used as recommended values for the calculation of the standard enthalpies of formation, $\Delta_f H_m^\circ$(g), of these compounds.

Enthalpies of Formation $\Delta_f H_m^\circ$(cr) and $\Delta_f H_m^\circ$(g). The thermochemistry of alkylureas in the condensed state (enthalpies of formation and heat capacities) is well-established. Reliable values of $\Delta_f H_m^\circ$(cr) are mostly available from the combustion experiments performed in Minsk laboratory and summarized by Kabo et al.[1] Some additional experimental results are cited in Table 3. To obtain $\Delta_f H_m^\circ$(g), we have used the selected values in this study of $\Delta_{cr}^{g}H_m$ (Table 3) and the known values for the enthalpies of formation in the solid state $\Delta_f H_m^\circ$(cr) in ref 1. Then a group-contribution method has been developed to predict values of the enthalpies of formation of alkylureas in both the gaseous and the solid phase as well as their enthalpies of sublimation.

Additive Calculations of Thermodynamic Properties of Urea Alkyl Derivatives. Despite experimental efforts reported in refs 1−11, the set of thermodynamic properties of alkylureas remains unique and different from others, especially for the restricted, especially for the number of species with branching of the alkyl chain. Traditional prediction methods based on constants related to the effective atoms (like Benson method[23]) or effective bonds (like Tatevski method[24]) are limited in their application because the number of linearly independent equations in such systems is less than the number of variables.[3,5] In our previous work,[5] we applied the effective atoms method[23,31] to the urea derivatives, using the nine additive variables such as those by Domalski and Hearing.[31] Two versions of the additive calculations were performed. The first one was for the set of the $\Delta_f H_m^\circ$(cr) of 10 entries: urea, 1-methylurea, 1-ethylurea, 1-isopropylurea, 1-*n*-butylurea, 1-*sec*-butylurea, 1-*tert*-butylurea, 1,1-dimethylurea, 1,1-diethylurea, and 1,3-di-*tert*-butylurea. The second calculation was for the same set, only excluding $\Delta_f H_m^\circ$(cr) of 1-ethylurea. The mean deviation of $\Delta_f H_m^\circ$(cr) calculated by the effective atoms increments from the experimental values amounted to 1.15 and 1.24 kJ·mol^{-1}, and even maximum deviations did not exceed the experimental error of (1 to 4) kJ·mol^{-1}. Nevertheless, one cannot rely on these calculations completely, as a slight change in the basic $\Delta_f H_m^\circ$(cr) set caused a large discrepancy in the values of additive contributions for some groups of atoms (see Table 1 in Supporting Information). That means that the derived group-contribution values are inconsistent from one subset of urea derivatives to another. One of the possible ways to overcome such complications was suggested by Domalski and Hearing,[31] where they treated together a broad set of experimental values on alkylureas, amides, and other related nitrogen-containing compounds. Such a procedure is more universal, and the group-contribution values became more robust. The mean deviation of $\Delta_f H_m^\circ$(cr) and $\Delta_f H_m^\circ$(g) calculated (see Tables 2 and 3 in Supporting Information) using the original Domalski and Hearing[31] increments from the experimental values (see Table 3) amounted to 4.1 and 5.6 kJ·mol^{-1}, respectively; however, maximum deviations exceed for some compounds their experimental error of (1 to 3) kJ·mol^{-1}. The most attractive advantage of the Domalski and Hearing[31] procedure is its universality; however, for this advantage the scheme is limited and offers less accuracy in prediction.

To obtain a specialized and consistent additive system based on the restricted or unique set of experimental data for alkyl carbamide derivatives (see Table 3), an incremental scheme that consists of the determination of increments for substitution of H atoms by CH_3 groups in the standard series have been used. This procedure has been shown to provide consistent results for enthalpies of formation in the solid state[3−5] as well as for enthalpies of sublimation.[2]

In the substitution procedure, urea is used as a reference compound to produce alkyl derivatives by subsequent substitution of CH_3 groups for H. For instance, the sequence of substitution yielding an alkyl substituted urea is of the form:



The formula for the physical−chemical property (P) calculations of alkylureas (AU) was

$$P(AU) = P(urea) + n_i\Delta P(CH_3)_N + n_j\Delta P(CH_3)_C + n_k\Delta P(CNC) + n_l\Delta P(CCN) + n_m\Delta P(CCC) \quad (4)$$

Table 4. Matrix of the Group Values and Calculated Values of Enthalpies of Formation and Sublimation for Alkyl Derivatives of Urea (in kJ·mol^{-1})

compound	$(CH_3)_N$	$(CH_3)_C$	CCN	CNC	CCC	$\Delta_f H^\circ_{m(cr)}$ calcd	Δ^{exp}_{add}	$\Delta^{g}_{cr} H_m$ calcd	Δ^{exp}_{add}	$\Delta_f H^\circ_{m(g)}$ calcd	Δ^{exp}_{add}
1-methylurea	1	0	0	0	0	−325.65	−2.15	93.93	1.97	−231.58	−0.32
1-ethylurea	1	1	1	0	0	−355.63	−2.17	96.81	2.49	−259.25	0.75
1-*n*-propylurea	1	2	1	0	1	−386.60		101.51	−0.11	−285.73	
1-isopropylurea	1	2	2	0	1	−386.03	−3.47	97.39	0.71	−289.41	−1.99
1-*n*-butylurea	1	3	1	0	2	−417.59	−1.91	106.22	0.48	−312.21	−2.29
1-isobutylurea	1	3	1	0	3	−418.00		103.93	−0.33	−314.70	
1-*sec*-butylurea	1	3	2	0	2	−417.02	3.82	102.09	−0.19	−315.89	4.59
1-*tert*-butylurea	1	3	3	0	3	−416.86	2.16	95.67	2.13	−322.06	5.16
1,1-dimethylurea	2	0	0	1	0	−316.24	−2.86	91.23	2.27	−224.14	−0.06
1,1-diethylurea	2	2	2	1	0	−376.20	4.00	96.98	−1.18	−279.48	3.08
1,3-dimethylurea	2	0	0	0	0	−317.70	4.00	91.86	−3.06	−225.56	0.66
1,3-diethylurea	2	2	2	0	0	−377.66	−2.14	97.61	−0.51	−280.90	−3.60
1,1-di-*tert*-butylurea	2	6	6	1	6	−498.66	−1.14	94.70	−1.10	−405.09	−3.01
average							± 2.7	± 1.3		± 2.3	

Table 5. Parameters for the Calculation of the Solid Enthalpy of Formation $\Delta_f H^\circ_m$(cr), Enthalpy of Sublimation $\Delta^g_{cr} H_m$, and Gaseous Enthalpy of Formation $\Delta_f H^\circ_m$(g) for Alkyl Derivative of Urea at T = 298.15K (in kJ·mol^{-1})

	value		
group contribution	$\Delta_f H^\circ_m$(cr)	$\Delta^g_{cr} H_m$	$\Delta_f H^\circ_m$(g)
NH_2CONH_2 (urea)	−330.6	96.0	−237.6
$(CH_3)_N$	7.95	−2.07	6.02
$(CH_3)_C$	−30.56	7.00	−23.99
CCN	0.58	−4.13	−3.68
CNC	1.46	−0.64	1.42
CCC	−0.42	−2.30	−2.49

where P(urea) is an appropriate property of urea ($\Delta_f H^\circ_m$(cr), $\Delta^g_{cr} H_m$, and $\Delta_f H^\circ_m$(g)); $\Delta P(CH_3)_N$ is an increment of H → CH_3 substitutions on a nitrogen atom; $\Delta P(CH_3)_C$ is an increment of H → CH_3 substitution on a carbon atom. The mutual influence of the introduced CH_3 groups (1,3-interactions) were taken into account through the three type of corrections by one to three interactions with polyvalent C and N atoms (appropriate contributions to the thermodynamic property are CNC, CCN, and CCC); n_i, n_j, n_k, n_l, and n_m are the quantities of the corresponding increments and correction. For example, for 1,3-dimethyl-1-isopropylurea, the calculation formula is

$$\mathrm{P(1,3\text{-}dimethyl\text{-}1\text{-}isopropylurea)} = \mathrm{P(urea)} + 3\Delta \mathrm{P(CH_3)_N} + 2\Delta \mathrm{P(CH_3)_C} + \Delta \mathrm{P(CNC)} + 2\Delta \mathrm{P(CCN)} + \Delta \mathrm{P(CCC)}$$

The matrix of the parameters, the calculated values of thermodynamic properties, and the divergence between experimental and additive values are listed in Table 4. The method of the polyfunctional least squares was used to evaluate the additive parameters. The values of the substitution increments and additional corrections for 1,3-interactions of the inserted CH_3 group, and polyvalent atoms of the skeleton were estimated from the selected experimental data set given in Table 5.

Validation of the Experimental Results Available for Alkylureas. The compilation of the selected experimental data on alkyl substituted ureas is listed in Table 3. One needs a criterion to assess the reliability of the experimental results. It has been possible in this work to evaluate independently the reliability of individual experimental data. One of the best flags to possible experimental errors is a large discrepancy between experimental and calculated values—especially if other, closely related compounds show no such discrepancy. In the frame of this work, we have evaluated additive parameters for the three thermodynamic properties simultaneously. Taking into account that all these three properties are not independent and that they are connected by the general equation:

$$\Delta_f H^\circ_m(\mathrm{g}) = \Delta_f H^\circ_m(\mathrm{cr}) + \Delta^g_{cr} H_m$$

it has been possible to check experimental data sets for each individual compound from the Table 2 for internal consistency by fitting them into the correlation and by minimizing of the deviation of predicted and experimental property. Using simultaneous optimization of the additive parameters for enthalpies of formation (in the gaseous and in the solid state) and enthalpy of sublimation, we have been able to assess the reliability of experimental values for each individual compound involved in the data treatment. Analysis of the results presented in Table 2

Table 6. Results of Ab Initio Calculation of the Standard Enthalpy of Formation $\Delta_f H^\circ_m$(g) for Alkylureas in the Gaseous Phase at 298.15 K

compound	$\Delta_f H^\circ_m$(g) exp kJ·mol^{-1}	$\Delta_f H^\circ_m$(g) atomization kJ·mol^{-1}	reaction 1 kJ·mol^{-1}	reaction 2 kJ·mol^{-1}	reaction 3 kJ·mol^{-1}	$\Delta_f H^\circ_m$(g)^a calcd kJ·mol^{-1}	(exp − calcd)^b kJ·mol^{-1}
urea	−237.6	−224.2	−234.8	−234.7	−234.7	−234.7	−2.9
1-methylurea	−231.9	−220.7	−231.9	−231.2	−231.2	−231.4	−0.5
1-ethylurea	−258.5	−250.9	−262.1	−261.4	−261.4	−261.6	3.1
1-*n*-propylurea		−272.7	−283.9	−283.2	−283.2	−283.4	
1-isopropylurea	−291.4	−285.1	−296.3	−295.5	−295.6	−295.8	4.4
1-*n*-butylurea	−313.7	−293.8	−304.3	−304.3	−305.1	−304.6	−9.1
1-isobutylurea		−303.2	−313.7	−313.7	−314.4	−313.9	
1-*sec*-butylurea	−311.3	−305.2	−316.5	−315.7	−315.7	−316.0	4.7
1-*tert*-butylurea	−319.1	−316.5	−327.7	−326.9	−326.9	−327.2	8.1
1,1-dimethylurea	−224.2	−215.9	−227.2	−226.4	−226.4	−226.7	2.5
1,1-diethylurea	−276.4	−276.4	−287.6	−286.8	−286.8	−287.1	10.7
1,3-dimethylurea	−224.9	−216.3	−227.5	−226.7	−226.7	−227.0	2.1
1,3-diethylurea	−284.4	−276.8	−288.0	−287.2	−287.2	−287.5	3.1
1,1-di-*tert*-butylurea	−408.1	−407.9	−418.3	−418.3	−419.1	−418.6	10.5

[a] Average value from the results in columns 4, 5, and 6. [b] The difference of columns 2 and 7.

shows that the average standard deviation of the selected experimental data taken into correlation and the average standard deviation between experimental and predicted values are at the same level of (1.3 to 2.7) $kJ\cdot mol^{-1}$ as the experimental uncertainty. In this context it was interesting to check some archival data available for the long-chained symmetrical dialkylureas. The experimental data for enthalpies of formation $\Delta_f H_m^\circ(cr)$ of 1,1-diheptylurea (-627.6 ± 5.4) $kJ\cdot mol^{-1}$, of 1,1-dioctylurea (-715.2 ± 4.6) $kJ\cdot mol^{-1}$, and of 1,1-didecylurea (-877.4 ± 7.1) $kJ\cdot mol^{-1}$ were measured using combustion calorimetry.[29,30] The calculations of the $\Delta_f H_m^\circ(cr)$ for these compounds with help of parameters listed in the Table 5 provide the values of (−624.0, −748.0, and −871.9) $kJ\cdot mol^{-1}$, respectively. Thus, the data for 1,1-diheptylurea and 1,1-didecylurea seem to be reliable (within the boundaries of their experimental uncertainties), but the difference between experimental and calculated enthalpy of the formation of -29.2 $kJ\cdot mol^{-1}$ for 1,1-dioctylurea indicates that the experimental data may be in error.

Quantum Chemical Calculations for Alkylureas. Results of ab initio molecular orbital methods for calculation of the enthalpy of formation of alkylureas have not been yet reported in the literature. In standard Gaussian *n* theories, theoretical enthalpies of formation are calculated through atomization reactions.[25] Raghavachari et al.[26] have proposed using a set of isodesmic reactions, the “bond separation reactions”, to derive theoretical enthalpies of formation. Isodesmic reactions conserve the number of types of bonds and should thus be an improvement on simple atomization reactions. Further enhancement in the calculation of enthalpies of formation should be provided by homodesmic reactions, which, in addition to the types of bonds, also conserve the hybridization of the atoms in the bond. We have calculated the enthalpies of formation of alkylureas with help from both standard atomization reactions as well as homodesmic reactions. For the latter method, we have chosen the following three reactions:

$$C_nH_{(2n+2)}N_2O + (n-1)CH_4 = C_1H_4N_2O + (n-1)C_2H_6 \tag{1}$$

$$C_nH_{(2n+2)}N_2O + (n+1)CH_4 = CH_3{-}CO{-}CH_3 + 2NH_3 + (n-2)C_2H_6 \tag{2}$$

$$C_nH_{(2n+2)}N_2O + (n+6)CH_4 = H_2O + 2NH_3 + (n+3)C_2H_6 \tag{3}$$

Using enthalpies of these reactions calculated by G3(MP2) and enthalpies of formation $\Delta_f H_m^\circ(g)$ for urea, methane, acetone, water, ammonia, and ethane recommended by Pedley et al.,[27] enthalpies of formation of alkylureas have been calculated (see Table 6). There are two possible arrangements (cis and trans) of alkyl substituents of nitrogen toward the double bond of the carbonyl group. The preliminary calculations revealed that the cis-isomer was energetically favored (e.g., for 1-methylurea the stabilizing effect was 5.6 $kJ\cdot mol^{-1}$). The latter conformation was used in all further calculations of alkylureas. Comparison of the calculated and experimental data is given in Table 6. Enthalpies of formation of alkylureas derived with help of the atomization procedure are systematically (about 10 $kJ\cdot mol^{-1}$) less negative than the experimental results. Substantial better agreement was obtained with help of isodesmic reactions 1−3. Despite the fact that several calculated enthalpies of formation of alkylureas deviate by (8 to 10) $kJ\cdot mol^{-1}$, the average deviation obtained by G3(MP2) accounts for 5 $kJ\cdot mol^{-1}$, and this value is close to the uncertainties of experimental values.

The additivity methods serve as valuable tool for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes. Improved additivity parameters and the correction terms were systematically revised and evaluated in this work using an updated database. The derived values can be applied to the prediction of the thermochemical properties of a broad range the organic compounds containing carbamide moiety.

Supporting Information Available:

Ten figures showing the experimental data of vapor pressures and three additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review June 15, 2005. Accepted November 1, 2005. V.N.E. gratefully acknowledges a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst).

JE050230Z