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Note

Correlation of thermochemical data for ureas with the degree of N-substitution

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Considerable interest is focussed on the thermochemistry of urea and N-alkyl and N-aryl substituted ureas in view of the significance of these compounds in biological systems. However, relatively few thermochemical data exist for urea and substituted ureas. For urea, Cox and Pilcher [1] have selected $\Delta_f H_m^\ominus(298\ \mathrm{K}) = -333.59 \pm 0.21$ kJ mol^{-1}, based on the static bomb calorimetry data of Aston and Messerley [2], Ruehrwein and Huffman [3] and Månsson and Sunner [4]. Cox and Pilcher [1] have also selected $\Delta_{sub} H_m^\ominus(\mathrm{urea}) = 87.9 \pm 2.1$ kJ mol^{-1} based on the vapour pressure/temperature data of Suzuki et al. [5] which in combination with the corresponding selected $\Delta_f H_m^\ominus$ value gives $\Delta_f H_m^\ominus(\mathrm{g})(\mathrm{urea}) = -245.6 \pm 2.1$ kJ mol^{-1}. Stull et al. [6] have tabulated $S_m^\ominus(298\ \mathrm{K})$, $\Delta_f G_m^\ominus(298\ \mathrm{K})$ and log K_p data for urea as derived by Ruehrwein and Huffman [3] and Suzuki et al. [5], but corresponding selected data are not provided. For urea nitrate, Stull et al. [6] have selected $\Delta_f H_m^\ominus(298\ \mathrm{K}) = -562.8$ kJ mol^{-1}, based on the calorimetric data of Médard and Thomas [7].

Standard enthalpies of formation are known for a limited range of N-alkyl and N-aryl substituted ureas: $R_1R_2NCONR_3R_4$ with R_1 = ethyl or phenyl, $R_2 = R_3 = R_4 = H$ [8]; $R_1 = R_3$ = methyl, R_2 = phenyl, R_4 = H [9]; $R_1 = R_2 = R_3$ = methyl, R_4 = H [9]; R_1 = methyl, R_2 = phenyl, R_3 = ethyl, R_4 = H [9]; R_1 = methyl, R_2 = tolyl, $R_3 = R_4$ = H [9]; $R_1 = R_2 = R_3 = R_4$ = ethyl [9]; $R_1 = R_2$ = phenyl, $R_3 = R_4$ = H [10]; $R_1 = R_2$ = phenyl, R_3 = ethyl, R_4 = H [10]; $R_1 = R_3$ = phenyl, $R_2 = R_4$ = methyl [10]; $R_1 = R_3$ = phenyl, R_2 = methyl, R_4 = ethyl [10]; $R_1 = R_3$ = heptyl or octyl, $R_2 = R_4$ = H [11]. All these data are assessed and tabulated by Stull et al. [6]. Recently, Davies et al. [12] have reported the standard enthalpy of formation of 1,3-dimethylurea as -312.1 ± 2.9 kJ mol^{-1}, as derived by classical static bomb calorimetry.

In view of the general lack of principal thermodynamic data for ureas, it is relevant to investigate correlations of existing data with urea structure,

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with the primary aim of estimating thermodynamic parameters for a homologous series of ureas.

Many progressive methodical attempts have been made to refine the available methods for the estimation of principal thermodynamic quantities. Many of these revised methods are based on a "group contribution" principle [13]—the compound of interest is considered as composed of a parent molecule that has been modified by substitution of specified atoms by appropriate groups to achieve the molecule in question. On this basis, some correlation between thermodynamic parameters and structure for a homologous urea series is expected. Linear relationships have been demonstrated to exist between $\Delta_{\text{vap}} H_{\text{m}}^{\ominus}$ and structure for a homologous series of hydrocarbons [14] and alcohols [15], and Laidler, Lovering and Nor [16–18] have proposed an elaborate scheme which correlates $\Delta_{\text{vap}} H_{\text{m}}^{\ominus}$ directly with molecular structure for many types of aliphatic, alicyclic and benzenoid compounds—bond contributions rather than group contributions are considered. However, this scheme has only limited demonstrated application to nitrogen-containing compounds.

A preliminary approach to the verification of a direct correlation between thermodynamic parameters for a urea and the number of N-substituents is to consider N-substitution in terms of the consequential bonding and non-bonding interactions established. The following fundamental equations form a prelude to a possible correlation proposal.

$$\Delta_{\text{f}} H_{\text{m}}^{\ominus} = \Delta_{\text{f}} H_{\text{m}}^{\ominus}(\text{g}) - \Delta_{\text{sub}} H_{\text{m}}^{\ominus} \tag{1}$$

$$\Delta_{\text{f}} H_{\text{m}}^{\ominus} = \Delta_{\text{f}} H_{\text{m}}^{\ominus}(\text{g}) - \Delta_{\text{fus}} H_{\text{m}}^{\ominus} - \Delta_{\text{vap}} H_{\text{m}}^{\ominus} \tag{2}$$

$$\Delta_{\text{f}} H_{\text{m}}^{\ominus} = \Delta H_{\text{B}} + \Delta H_{\text{NB}} - \Delta_{\text{fus}} H_{\text{m}}^{\ominus} - \Delta_{\text{vap}} H_{\text{m}}^{\ominus} \tag{3}$$

where $\Delta_{\text{f}} H_{\text{m}}^{\ominus}(\text{g})$, $\Delta_{\text{sub}} H_{\text{m}}^{\ominus}$, $\Delta_{\text{fus}} H_{\text{m}}^{\ominus}$ and $\Delta_{\text{vap}} H_{\text{m}}^{\ominus}$ are the standard enthalpies of formation of a urea in the gaseous state and the corresponding standard enthalpies of sublimation, fusion and vaporisation, respectively. Following the terminology of Allen [19], ΔH_{B} represents the sum of the bonded interactions and ΔH_{NB} represents the sum of the non-bonded interactions, with both of these terms referenced to the ideal gas phase. If steric interactions are ignored and for a maximum of one N-substituent on each of the N atoms in the general structure HRNCONR′H, then

$$\Delta H_{\text{NB}} = \Delta\text{NO}_{\text{d}}\text{N} + 2\Gamma\text{NC}_{\text{d}}\text{O}_{\text{d}} + \Gamma\text{NC}_{\text{d}}\text{N} + x\Gamma\text{CNC}_{\text{d}} \tag{4}$$

where $\Delta\text{NO}_{\text{d}}\text{N}$, $\Gamma\text{NC}_{\text{d}}\text{O}_{\text{d}}$, $\Gamma\text{NC}_{\text{d}}\text{N}$ and $\Gamma\text{CNC}_{\text{d}}$ are the relevant Allen parameters [19] for the urea skeleton with x N-alkyl substituents. Because $\Delta\text{NO}_{\text{d}}\text{N}$, $\Gamma\text{NC}_{\text{d}}\text{O}_{\text{d}}$ and $\Gamma\text{NC}_{\text{d}}\text{N}$ are essentially independent of the degree of N-substitution

$$\Delta_{\text{f}} H_{\text{m}}^{\ominus} - \Delta H_{\text{B}} + \Delta_{\text{fus}} H_{\text{m}}^{\ominus} + \Delta_{\text{vap}} H_{\text{m}}^{\ominus} = \Delta H\sigma + x\Gamma\text{CNC}_{\text{d}} \tag{5}$$

$$\Delta H\sigma = \Delta\text{NO}_{\text{d}}\text{N} + 2\Gamma\text{NC}_{\text{d}}\text{O}_{\text{d}} + \Gamma\text{NC}_{\text{d}}\text{N} \tag{6}$$

TABLE 1

Thermodynamic data for N-methyl ureas

$R_1R_2NCONR_3R_4$				x	$\Delta_f H_m^\ominus$ (kJ mol^{-1})	ΔH_B (kJ mol^{-1})	$\Delta_{fus} H_m^\ominus$ (kJ mol^{-1})	$\Delta_{vap} H_m^\ominus$ (kJ mol^{-1})
R_1	R_2	R_3	R_4					
H	H	H	H	0	−333.6 [a]	−4.9 [b]	+13.5 [c]	+74.4 [d]
CH_3	H	H	H	1	−327.7 [e]	+18.5 [b]	+14.0 [c]	+74 [f]
CH_3	H	CH_3	H	2	−312.1 [g]	+41.8 [b]	+12.4 [d]	+74 [f]
CH_3	CH_3	CH_3	H	3	−330.5 [h]	+65.1 [b]	+14 [f]	+74 [f]

[a] From ref. 1.

[b] Calculated using Allen bond energies [1] (Table 51, p. 593).

[c] From ref. 20.

[d] Based on $\Delta_{sub} H_m^\ominus$(urea) = 87.9 kJ mol^{-1} [5].

[e] From ref. 21.

[f] Estimated.

[g] From ref. 12.

[h] From ref. 9.

For $x > 2$, $\Delta H\sigma$ is dependent on x and additional Allen parameters must be included. Thus for $x = 3$

$$\Delta H\sigma = \Delta NO_dN + 2\Gamma NC_dO_d + \Gamma NC_dN + \Gamma CNC + \Delta^N_{CCCd} \tag{7}$$

and for $x = 4$

$$\Delta H\sigma = \Delta NO_dN + 2\Gamma NC_dO_d + \Gamma NC_dN + 2\Gamma CNC + 2\Delta^N_{CCCd} \tag{8}$$

Thus, for a di-substituted urea of general structure HRNCONR′H, this simplistic thermodynamic model suggests a linear relationship between empirical thermodynamic parameters for a urea and the degree of N-substitution thereof, with the corresponding slope and intercept reflecting the magnitude of the non-bonded interactions. For more highly substituted ureas, $x = 3$ and $x = 4$, deviations from such a linear relationship are expected of magnitude equivalent to $(\Gamma_{CNC} + \Delta^N_{CCCd})$ and $2(\Gamma_{CNC} + \Delta^N_{CCCd})$ respectively. It is difficult to test this correlation as, even for a systematic series of N-methyl ureas, incomplete thermodynamic data are available (Table 1). Estimates are provided for the enthalpy of fusion of 1,1,3-trimethylurea; the enthalpies of vaporisation of 1-methylurea 1,3-dimethylurea and 1,1,3-trimethylurea are estimated to be equal to that of urea. A linear relationship appears to exist between $[\Delta_f H_m^\ominus - \Delta H_B + \Delta_{fus} H_m^\ominus + \Delta_{vap} H_m^\ominus]$ ($[y]$) and x ($x \not> 2$) with the line of "best fit", $y = -13.35x - 242.15$. For N,N,N'-trimethylurea, $x = 3$ and the value of the combined ordinate terms, $[y]$, deviates from the line of best fit by -25.4 kJ mol^{-1}. The Allen parameter $\Gamma_{CNC} = -18$ kJ mol^{-1} [19]. Δ^N_{CCCd} is not known but may be taken as the mean of $(\Delta^N_{CNC} + \Delta^N_{CCd}) = -12.0$ kJ mol^{-1}, which is not in agreement with the increment calculated previously. However, based on this model, $[\Delta_f H_m^\ominus - \Delta H_B + \Delta_{fus} H_m^\ominus + \Delta_{vap} H_m^\ominus]$ for $N,N,N'N'$-tetramethylurea is calculated to be -346.4 kJ mol^{-1}. For this urea, $\Delta H_B = 88.4$ kJ mol^{-1}, $\Delta_{\text{fus}} H_m^\ominus$ and $\Delta_{\text{vap}} H_m^\ominus$ are estimated as 14 and 74 kJ mol^{-1} respectively and, hence, $\Delta_f H_m^\ominus$ is calculated to be -346.0 kJ mol^{-1}.

Refinement of this simplistic model is possible via realistic methods for the derivation of the fusion and vaporisation enthalpies for an *N*-methylurea. For an *N*-methylurea (Φ), the vaporisation enthalpy, $\Delta_{\text{vap}} H_m^\ominus(\Phi)$ is expected to increase with molar mass of the urea according to an equation of the type

$$\Delta_{\text{vap}} H_m^\ominus(\Phi) = \Delta_{\text{vap}} H_m^\ominus + x\delta \tag{9}$$

where δ represents a constant increment in $\Delta_{\text{vap}} H_m^\ominus$ resulting from the addition of a methyl group to the urea structure. For a wide range of aliphatic and aromatic compounds, Laidler, Lovering and Nor [16–18] have estimated the methyl group contribution to $\Delta_{\text{vap}} H_m^\ominus$ as 6.2 kJ mol^{-1}. In the absence of alternative data, the increment δ, pertaining to a homologous series of ureas, may be taken as 6.2 kJ mol^{-1}. The line of "best fit" for $[\Delta_f H_m^\ominus - \Delta H_B + \Delta_{\text{fus}} H_m^\ominus + \Delta_{\text{vap}} H_m^\ominus + x\delta]$ ($[y']$) versus x ($x \not> 2$) is $y' = -7.15x - 242.15$. The deviation increment for $\Delta_f H_m^\ominus$ (*N*,*N*,*N*′-trimethylurea) is, once again, -25.4 kJ mol^{-1}, and following the calculation procedures described previously, $\Delta_f H_m^\ominus$ (*N*,*N*,*N*′,*N*′-tetramethylurea) $= -321.6$ kJ mol^{-1}.

Further refinement of the model requires calculation of the fusion enthalpies of *N*,*N*,*N*′-trimethylurea and *N*,*N*,*N*′,*N*′-tetramethylurea based on the relationship $\Delta_{\text{fus}} H_m^\ominus = \Delta_{\text{fus}} S_m^\ominus T_m$, where T_m is the relevant melting point. Bondi [22] has given elaborate empirical methods for the calculation of fusion entropy based on molecular structure, but these procedures have not been extended to nitrogen-containing compounds.

Overall, these simplistic thermodynamic models appear to have considerable merit in the prediction of standard formation enthalpies of multi-substituted ureas.

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