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The thermochemistry of 1,3-dimethylurea and 1,3-dimethylurea nitrate

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Abstract

Using an adiabatic oxygen combustion static bomb calorimeter, the standard enthalpy of formation of 1,3-dimethylurea has been determined as $-(312.1 \pm 2.8)$ kJ mol^{-1}. Solution calorimetry and pK_a measurements yield the standard enthalpy of formation of 1,3-dimethylurea nitrate and the enthalpy of protonation of aqueous 1,3-dimethylurea as $-(540.7 \pm 2.8)$ kJ mol^{-1} and $+(1.56 \pm 0.60)$ kJ mol^{-1} respectively.

INTRODUCTION

Considerable interest is focused on the thermochemistry of urea and *n*-alkyl and *n*-aryl substituted ureas, in view of the significance of these compounds in biological systems. Further, it is established [1] that urea is a useful additive in the combustion calorimetry of sulphur compounds in order to effect oxidation of sulphur to the +6 state. Also, urea has been suggested [2] as an alternative standard to hippuric acid for combustion bomb calorimetry of nitrogen-containing compounds.

Relatively few thermochemical data exist for urea and substituted ureas. For urea, Cox and Pilcher [2] have selected $\Delta_f H_m^{\ominus}(298\ \text{K}) = -(333.59 \pm 0.21)$ kJ mol^{-1} based on static bomb calorimetry data of Aston and Messerley, [3] Ruehrwein and Huffman, [4] Månsson and Sunner [1] and, more recently, Johnson [5] $-(333.39 \pm 0.17)$ kJ mol^{-1}. Cox and Pilcher [2] have also selected $\Delta_{sub} H_m^{\ominus}(\text{urea}) = 87.9 \pm 2.1$ kJ mol^{-1} based on vapour pressure/temperature data of Suzuki et al. [6] which, in combination with the corresponding selected $\Delta_f H_m^{\ominus}$, gives $\Delta_f H_m^{\ominus}(\text{g})(\text{urea}) = -(245.6 \pm 2.1)$ kJ mol^{-1}. Stull et al. [7] have tabulated $S_m^{\ominus}(298\ \text{K})$, $\Delta_f G_m^{\ominus}(298\ \text{K})$ and log K_p data for urea as derived by Ruehrwein and Huffman [4] and Suzuki et al. [6] but corresponding selected data are not provided. For urea nitrate Stull et al. [7] have selected $\Delta_f H_m^{\ominus}(298\ \text{K}) = -562.8$ kJ mol^{-1}, based on calorimetric data of Médard and Thomas [8].

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Standard enthalpies of formation are known for a limited range of *n*-alkyl and *n*-aryl substituted ureas, $R_1R_2NCONR_3R_4$: R_1 = ethyl or phenyl, $R_2 = R_3 = R_4$ = H [9]; $R_1 = R_3$ = methyl, R_2 = phenyl, R_4 = H [10]; $R_1 = R_2 = R_3$ = methyl, R_4 = H [10]; R_1 = methyl, R_2 = phenyl, R_3 = ethyl, R_4 = H [10]; R_1 = methyl, R_2 = tolyl, $R_3 = R_4$ = H [10]; $R_1 = R_2 = R_3 = R_4$ = ethyl; $R_1 = R_2$ = phenyl, $R_3 = R_4$ = H [11]; $R_1 = R_2$ = phenyl, R_3 = ethyl, R_4 = H [11]; $R_1 = R_3$ = phenyl, $R_2 = R_4$ = methyl [11]; $R_1 = R_3$ = phenyl; R_2 = methyl, R_4 = methyl [11]; $R_1 = R_3$ = heptyl or octyl, $R_2 = R_4$ = H [12]. All these were assessed and tabulated by Stull et al. [7].

This paper reports the standard enthalpy of formation of 1,3-dimethylurea as derived by classical static bomb calorimetry, and the standard enthalpy of formation of 1,3-dimethylurea nitrate and the enthalpy of protonation of aqueous 1,3-dimethylurea as derived by solution calorimetry and pK_a measurements respectively.

EXPERIMENTAL

1,3-Dimethylurea was obtained from Koch–Light Labs. (puriss) and was fractionally crystallised from propan-2-ol. The purity was determined as > 99.9% using differential scanning calorimetry to scan the fusion range with subsequent analysis of the fraction melted/temperature profile [13]. (T_m = 377.5 K; lit. [14] T_m = 376.8 K).

Urea, (AnalaR, B.D.H. Ltd.) was used without further purification.

1,3-Dimethylurea nitrate was prepared by slowly adding concentrated nitric acid (Aristar, B.D.H.) to a saturated aqueous solution of 1,3-dimethylurea. The resultant solution was reduced in volume by rotary evaporation and then cooled in an ice bath; the crystalline 1,3-dimethylurea nitrate was filtered off and washed with diethylether. Analysis by titration against standardised sodium hydroxide solution indicated a purity of 99.7%.

Calorimeters

The solution calorimeter system (LKB 8700) and operating procedures have been described previously [15]. All ampoule filling was carried out under dry nitrogen.

The adiabatic bomb calorimeter was a commercial system (CB-110, Gallenkamp Ltd.) with the following modifications: the thermistor bridge was replaced by a quartz crystal thermometer (2801A, Hewlett–Packard) with a digital printer (S23562A, Hewlett–Packard) and analogue output connected to a chart recorder; the original bomb was replaced (101a 6028, Parr Instruments Co.) and the calorimeter vessel replaced with one made from copper. The corrected temperature rise was evaluated graphically, according to well established [16] procedures.

pK_a *Measurements*

The titration of dilute aqueous nitric acid with solid 1,3-dimethylurea was followed using a glass electrode (Electronic Instruments Ltd.) with internal reference, and a digital pH meter (801, Orion Research Inc.). A thin walled glass vessel containing approximately 150 g of solution was immersed in a water bath, the temperature being maintained at 298.15 ± 0.02 K. The solution was stirred through the insulated top of the titration cell which also contained holes for the glass electrode and sample addition. Before each titration series, the pH meter was calibrated at pH = 4.008 and pH = 3.557 using 0.05 molal potassium hydrogen phthalate and saturated potassium hydrogen tartrate as standards [17]. Measurements were carried out on urea to test procedures prior to 1,3-dimethylurea titrations.

RESULTS AND DISCUSSION

Combustion calorimetry

Results of eight determinations of the standard enthalpy of combustion of 1,3-dimethylurea are given in Table 1. The meaning of the symbols are as follows: ΔT_{COR}, the corrected temperature rise, obtained by graphical extrapolation of the recorded initial and final periods; q_{TOT}, total observed energy change; $q_{(\mathrm{COR+B})}$, energy corrections to standard state process + energy correction for benzoic acid promoter; ε(standard), the effective energy equivalent of the calorimeter system; $\Delta_c u_g^\ominus$, the standard specific energy of combustion. Initially, during these experiments, benzoic acid was used as a combustion promoter; however, in the latter half of the series, the

TABLE 1

The enthalpy of combustion of crystalline 1,3-dimethylurea

$m[\mathrm{CO(NHMe)_2}]$ (g)	$m(\mathrm{C_6H_5CO_2H})$ (g)	ΔT_{COR} (K)	$-q_{\mathrm{TOT}}$ (J)	$-q_{(\mathrm{COR+B})}$ (J)	$-\Delta u_{\mathrm{C}}^\ominus$ (kJ $\mathrm{g^{-1}}$)
0.90823	0.57164	4.1665	35937	15157	22.880
0.97402	0.22945	3.2859	28342	6118	22.817
0.96468	0.22348	3.2433	27974	5974	22.805
1.03505	0.21724	3.4129	29437	5790	22.846
0.91176	0	2.4220	20890	74	22.831
1.03884	0	2.7532	23747	90	22.773
0.99151	0	2.6264	22653	77	22.769
0.97975	0	2.6019	22442	80	22.824

promoter was omitted. Calculated values for these parameters are as follows: $\varepsilon = 8625.3 \pm 2.6$ J K^{-1}; $\Delta_c u_g^{\ominus} = -22.818 \pm 0.031$ kJ g^{-1}; $\Delta_c U_m^{\ominus} = -2010.5 \pm 2.8$ kJ mol^{-1}.

From the derived value of the standard enthalpy of combustion, $\Delta_c H_m^{\ominus} = -2011.7 \pm 2.8$ kJ mol^{-1} for the reaction

$$C_3H_8N_2O(cr) + \tfrac{9}{4}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) + N_2(g)$$

using [18] $\Delta_f H_m^{\ominus}(H_2O)(l)(298.15\ K) = -285.830 \pm 0.042$ kJ mol^{-1} and [18] $\Delta_f H_m^{\ominus}(CO_2)(g)(298.15\ K) = -393.51 \pm 0.13$ kJ mol^{-1}, the standard enthalpy of formation of 1,3-dimethylurea is derived as $\Delta_f H_m^{\ominus}(CO(NHMe)_2)$ (c)(298.15 K) $= -312.1 \pm 2.8$ kJ mol^{-1}.

*p*K*a* Measurements

Two series of measurements for both urea and 1,3-dimethylurea were made. In each case pH readings, after addition of base, were converted to "hydrogen ion molalities" using the Guntelberg approximation to the Debye–Huckel equation

$$-\ln \gamma_{\pm} = \log_{10} A I^{1/2}/(1 + B I^{1/2})$$

where $A = 0.5108$; $B = 2.9574$ $kg^{1/2}$ $mol^{-1/2}$, respectively, $I = 0.5\ \Sigma m_i z_i^2$, and m_i and z_i are the molalities and charge of the ith ion. The change in calculated hydrogen ion molality was assumed to be caused by protonation of the base. Thus, knowing the overall concentration of base and the initial hydrogen ion molality, the observed equilibrium constant K' for the dissociation of the conjugate acid is derived from

$$K' = m_{\mathrm{BASE}} m_{\mathrm{H^+}} \gamma_{\mathrm{H^+}} / m_{\mathrm{BASE \cdot H^+}}$$

Extrapolation of this equilibrium constant to zero base concentration yields the true equilibrium constant. Using this method, only changes in pH are significant; thus errors in the determination of the hydrogen ion molality

TABLE 2

The enthalpy of solution of $CO(NHMe)_2$ in 1 mol dm^{-3} HNO_3 at 298.15 K

$m[CO(NHMe)_2]$ (g)	q	$\Delta_l H_m$ (kJ mol^{-1})
0.24689	35.7	1.540
0.24323	36.2	1.480
0.27257	32.3	1.510
0.30795	28.6	1.499
0.16629	53.0	1.476
0.23167	38.0	1.398
0.21090	41.8	1.516

$\Delta_l H_m = +1.488 \pm 0.042$ kJ mol^{-1}.

TABLE 3

The enthalpy of solution of $CO(NHMe)_2 \cdot HNO_3(c)$ in 0.97 mol dm^{-3} HNO_3 at 298.15 K

$m[CO(NHMe)_2 \cdot HNO_3]$ (g)	q'	$\Delta_2 H_m$ (kJ mol^{-1})
0.40573	36.1	23.355
0.44615	32.9	23.386
0.44479	33.0	23.496
0.49545	29.6	23.400
0.48744	30.1	23.358
0.44313	33.1	23.415

$\Delta_2 H_m = +23.402 \pm 0.054$ kJ mol^{-1}.

and K' are partially eliminated. At low base concentrations, random errors in the pH measurement have a large effect on K', thus when extrapolating to give the true equilibrium constant, measurements were weighted inversely with the estimated uncertainty in K' arising from a constant random error in pH. The values of pK_a urea and 1,3-dimethylurea were thus determined as 0.14 ± 0.02 and 0.17 ± 0.02 respectively. Our value for urea is in good agreement with that given by Wolley and Hepler [19] (0.10 ± 0.10). pK_a values for urea have also been reported by Perrin [20] and range from 0.10 to 0.40.

Solution calorimetry

The results of four series of measurements are given in Tables 2–5 and correspond to the calorimetric reactions

$$CO(NHMe)_{2(cr)} + [qHNO_3 + 55.5qH_2O]_{(sln)}$$

$$\xrightarrow{\Delta_1 H_m} [qHNO_3 + 55.5qH_2O + CO(NHMe)_2]_{(sln)} \quad (1)$$

$$CO(NHMe)_2 \cdot HNO_{3(cr)} + [q'HNO_3 + 57.2q'H_2O]_{(sln)}$$

$$\xrightarrow{\Delta_2 H_m} [(q'+1)HNO_3 + 57.2q'H_2O + CO(NHMe)_2]_{(sln)} \quad (2)$$

TABLE 4

The enthalpy of solution of $CO(NHMe)_2(c)$ in water at 298.15 K

$m[CO(NHMe)_2]$ (g)	P[a]	$\Delta_3 H_m$ (kJ mol^{-1})
0.26130	1866	0.702
0.26453	1843	0.780
0.28943	1684	0.694
0.26176	1862	0.758
0.25142	1939	0.747

[a] Mol. ratio, $H_2O:CO(NHMe)_2$. $\Delta_3 H_m = +0.736 \pm 0.046$ kJ mol^{-1}.

TABLE 5

The enthalpy of solution of $CO(NHMe)_2 \cdot HNO_3(c)$ in water at 298.15 K

$m[CO(NHMe)_2 \cdot HNO_3]$ (g)	p' [a]	$\Delta_4 H_m$ (kJ mol^{-1})
0.41005	2039	22.548
0.31225	2678	22.541
0.37076	2255	22.485
0.33243	2515	22.513
0.27282	3065	22.576
0.22921	3648	22.502
0.34324	2436	22.535

[a] Mol. ratio, $H_2O : CO(NHMe)_2 \cdot HNO_3$. $\Delta_4 H_m = +22.529 \pm 0.028$ kJ mol^{-1}.

$$CO(NHMe)_{2(cr)} + \infty H_2O \xrightarrow{\Delta_3 H_m} CO(NHMe)_{2(\infty H_2O)} \tag{3}$$

$$CO(NHMe)_2 \cdot HNO_{3(cr)} + \infty H_2O \xrightarrow{\Delta_4 H_m} CO(NHMe)_{2(\infty H_2O)} + HNO_{3(\infty H_2O)} \tag{4}$$

For reactions (1)–(4) the solute masses correspond to infinite dilution conditions. From reactions (1) and (2), neglecting the enthalpy of dilution of nitric acid from the final states of reaction (1) to reaction (2), the standard enthalpy of formation of 1,3-dimethylurea nitrate is given by

$$\begin{aligned}&\Delta_f H_m^{\ominus}(CO(NHMe)_2 \cdot HNO_3)(c)(298.15\ K)\\ &= \Delta_1 H_m - \Delta_2 H_m + \Delta_f H_m^{\ominus}(CO(NHMe)_2)(c)(298.15\ K)\\ &\quad + \Delta_f H_m^{\ominus}(HNO_3)(aq)(1\ mol\ dm^{-3})(298.15\ K)\end{aligned} \tag{5}$$

Using the values -312.1 ± 2.8 kJ mol^{-1} and -206.68 ± 0.46 kJ mol^{-1} for the standard enthalpies of formation of crystalline 1,3-dimethylurea and aqueous 1 mol dm^{-3} nitric acid [21] we obtain

$$\Delta_f H_m^{\ominus}(CO(NHMe)_2 \cdot HNO_3)(c)(298.15\ K) = -540.7 \pm 2.8\ kJ\ mol^{-1}$$

For reaction (1) conditions, the fraction α of 1,3-dimethylurea that is unprotonated in the final state may be estimated. Using $pK_a = 0.17$ and an estimate of the activity coefficient quotient

$$(\gamma_{\pm,HNO_3} \times \gamma_{BASE})/(\gamma_{\pm\ BASE \cdot HNO_3}) = 0.862 \tag{6}$$

(This value is based on the observed $\gamma_{\pm,HNO_3}$ at 1 mol dm^{-3})

$\alpha = 0.430 \pm 0.050$

The following thermochemical equations apply for the dissolution of 1,3-dimethylurea in nitric acid

$$\begin{aligned}&CO(NHMe)_{2(cr)} + (1-\alpha)HNO_{3(aq)}\\ &\xrightarrow{\Delta_A H_m} [(1-\alpha)CO(NHMe)_2 \cdot H^+ + \alpha CO(NHMe)_2 + (1-\alpha)NO_3^-]_{(aq)}\end{aligned} \tag{7}$$

$$(1-\alpha)\mathrm{HNO}_{3(\mathrm{aq})} \xrightarrow{\Delta_B H_m} [(1-\alpha)\mathrm{HNO}_3]_{\infty\mathrm{H_2O}} \qquad (8)$$

$$\mathrm{CO(NHMe)}_{2(\mathrm{c})} \xrightarrow{\Delta_C H_m} [(1-\alpha)\mathrm{CO(NHMe)}_2 + \alpha\mathrm{CO(NHMe)}_2]_{\infty\mathrm{H_2O}} \qquad (9)$$

For the protonation of $(1-\alpha)$ moles of base, corresponding to the overall reaction (7) + (8) + (9)

$$[(1-\alpha)\mathrm{CO(NHMe)}_2]_{\infty\mathrm{H_2O}} + [(1-\alpha)\mathrm{H}^+]_{\infty\mathrm{H_2O}} \rightarrow [(1-\alpha)\mathrm{CO(NHMe)}_2 \cdot \mathrm{H}^+]_{\infty\mathrm{H_2O}} \qquad (10)$$

where $\Delta_A H_m$ and $\Delta_C H_m$ corresponding tq $\Delta_1 H_m$ and $\Delta_3 H_m$ (Tables 2 and 4) for 1 mole of base, and the enthalpy of dilution $\Delta_B H_m$ is taken as $-0.51(1-\alpha)$ kJ mol^{-1}. The resultant molar protonation enthalpy of aqueous 1,3-dimethylurea, $\Delta_P H_m^{\ominus} = 1.86 \pm 0.20$ kJ mol^{-1}. Using the results of reactions (2) and (4) (Tables 2 and 3) and following similar principles, an independent value for the enthalpy of protonation is derived: $\Delta_P H_m^{\ominus} = 1.26 \pm 0.12$ kJ mol^{-1}. No literature $\Delta_P H_m$ value exists for comparison purposes. For the final state of reaction (2), an estimated $\alpha = 0.444 \pm 0.50$ corresponds with that found for reaction (1). Therefore, the assumption of the equivalence between the final states of reactions (1) and (2) appears justified.

Because the two values of $\Delta_P H_m^{\ominus}$ differ by more than the sums of the corresponding uncertainties, it appears that a small systematic error is associated with one or both results. However we propose a 'best' value $\Delta_P H_m^{\ominus} = 1.56 \pm 0.60$ kJ mol^{-1}. Although the final state of reaction (4) contains a low concentration of solute, we estimate that $\alpha = 0.970 \pm 0.009$; thus three per cent of the base remains protonated. Using 1.56 kJ mol^{-1} for the enthalpy of protonation, $\Delta_4 H_m^{\ominus}$ may be corrected and the standard enthalpy of formation of 1,3-dimethylurea nitrate evaluated

$$\mathrm{CO(NHMe)_2HNO}_{3(\mathrm{c})} \xrightarrow{\Delta_4 H_m^{\ominus}} [\mathrm{CO(NHMe)}_2 + \mathrm{HNO}_3]_{\infty\mathrm{H_2O}}$$

Taking $\Delta_f H_m^{\ominus}(\mathrm{CO(NHMe)_2})(\mathrm{c})(298.15\ \mathrm{K}) = -312.1 \pm 2.8$ kJ mol^{-1} and $\Delta_f H_m^{\ominus}(\infty\mathrm{H_2O})(298.15\ \mathrm{K})$ [21] $= -207.19 \pm 0.46$ kJ mol^{-1} and $\Delta_3 H_m$ for the enthalpy of solution of 1,3-dimethylurea in water, we obtain

$$\Delta_f H_m^{\ominus}(\mathrm{CO(NHMe)_2HNO_3})(\mathrm{c})(298.15\ \mathrm{K}) = -541.0 \pm 2.8\ \mathrm{kJ\ mol^{-1}}$$

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