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A calorimetric study of *N*,*N*-diethyl-*N*′-furoylthiourea and *N*,*N*-diisobutyl-*N*′-furoylthiourea

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The standard (p^o = 0.1 MPa) molar enthalpies of combustion in oxygen, at T = 298.15 K, were measured by rotative bomb calorimetry for crystalline *N*,*N*-diethyl-*N*′-furoylthiourea, (2-C_4H_3O)CONHCSN(C_2H_5)$_2$, HFET, and *N*,*N*-diisobutyl-*N*′-furoylthiourea, (2-C_4H_3O)CONHCSN(*iso*-C_4H_9)$_2$, HFIB. The standard molar enthalpies of sublimation of both HFET and HFIB were measured by high-temperature Calvet microcalorimetry. These values were used to derive the standard molar enthalpies of formation of the compounds, in their crystalline and gaseous phases.

	$-\Delta_c u^o$(cr)/J · g^{-1}	$\Delta_{cr}^{g} H_m^o$/kJ · mol^{-1}
(2-C_4H_3O)CONHCSN(C_2H_5)$_2$	27505.0 ± 4.5	132.0 ± 3.5
(2-C_4H_3O)CONHCSN(*iso*-C_4H_9)$_2$	31218.8 ± 2.0	141.7 ± 5.6

KEYWORDS: *N*,*N*-diethyl-*N*′-furoylthiourea; *N*,*N*-diisobutyl-*N*′-furoylthiourea; enthalpy of combustion; enthalpy of sublimation; enthalpy of formation

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1. Introduction

Acylchalcogenoureas are good chelating ligands due to there ability to act as selective complexing agents and so are widely used in analytical applications,[1] in heavy-metal hydrometallurgy,[2] in trace enrichment and in chromatographic separation of metals.[3] Its complexes are easily extracted by apolar solvents and separated by chromatographic techniques, allowing efficient yield even in low residual metal concentrations. Moreover, it is known that the nature of the acyl group and terminal nitrogen atom substituents are important to the coordination ability of the ligands.[4] Therefore, a systematic study of these type of molecules with different substituents has been carried and although a large number of papers[1–6] have been devoted to the synthesis and physical properties of these kinds of ligands and their complexes, very few studies were published[7] on their thermochemical properties, either in the gaseous or condensed phases.

This paper, which is a part of a broader research programme on the energetic properties of acylchalcogenoureas and their metal complexes, presents a thermochemical study of *N*,*N*-diethyl-*N*′-furoylthiourea (HFET) and *N*,*N*-diisobutyl-*N*′-furoylthiourea (HFIB), both in the condensed and gaseous phases.

2. Experimental

Although the synthesis of monoalkylfuroylthioureas, RCO NH CS NHR′, was already described by Douglass *et al*.,[8] the preparation of dialkyl derivatives, RCO NH CS NR′$_2$, has not been reported before.

The *N*,*N*-diethyl-*N*′-furoylthiourea, (2-C_4H_3O)CONHCSN(Et)$_2$ (HFET), was prepared according to the method previously reported for other acylthioureas[8] by adding an acetone solution of 0.10 mol (9.8 g) of potassium thiocianate to an acetone solution of 0.11 mol (13.9 g) of 2-furoyl chloride. After mixture, a cold acetone solution of 0.14 mol (10.3 g) of diethylamine was added and stirred for another 0.5 h, after which time it was poured into a water/ice mixture. The filtrate was recrystallized from an ethanol/water mixture, yielding white crystals with a melting temperature of $T_{fus} = 373$ K–375 K.

The *N*,*N*-diisobutyl-*N*′-furoylthiourea, (2-C_4H_3O)CONHCSN(*i*But)$_2$ (HFIB), was prepared by the same procedure: an acetone solution of 0.10 mol (9.9 g) of potassium thiocianate was added to an acetone solution of 0.11 mol (13.9 g) of 2-furoyl chloride. After mixture, a cold acetone solution of 0.12 mol (15.2 g) of diisobutylamine was added and stirred for another 0.5 h, after which it was poured into a water/ice mixture. The filtrate was washed with *n*-pentane and recrystallized from an ethanol/water mixture, yielding white crystals with a melting temperature of $T_{fus} = 360$ K–361 K.

The enthalpies of combustion for both compounds were measured using a rotating bomb calorimeter previously described.[9] The experiments were performed in a platinum-lined bomb of internal volume 0.337 dm^3. Water was added to the calorimeter from a weighed *perspex* vessel and a correction to the energy equivalent was made to account for the deviation in the mass of water from 4059.0 g. The ignition temperatures were chosen in such a way to have a final temperature as close as possible to 298.15 K. In each experiment, rotation started at a time from the main period when the temperature rise was

about 63 per cent of the total expected, so the frictional work due to bomb rotation could be included in the corrections for the heat leakage and work of stirring, in accordance with the procedures of Good *et al.*[10]

The system described above was calibrated by burning benzoic acid pellets (Bureau of Analyzed Samples, Thermochemical Standard, BCS-CRM-190r) with a specific heat of combustion under certificate conditions of $-(26432.3 \pm 3.8)\ \mathrm{J \cdot g^{-1}}$. This procedure led, from eight experiments, to an energy equivalent of $\varepsilon(\mathrm{calor}) = (20690.2 \pm 3.3)\ \mathrm{J \cdot K^{-1}}$ referred to a 4059.0 g mass of water. The uncertainty given corresponds to the standard deviation of the mean. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. The massic energy of combustion of the cotton thread used, of empirical formula $CH_{1.686}O_{0.843}$, was $\Delta_c u^o = -16250\ \mathrm{J \cdot g^{-1}}$.[11] The corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$,[12] for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ HNO_3(aq) from gaseous N_2 and O_2, and liquid H_2O. The relative atomic masses used were those recommended by the IUPAC Commission in 1995.[13] The calorimetric system was tested by burning thiantrene pellets, ($C_{12}H_8S_2$), giving a massic energy of combustion after eight experiments of $\Delta_c u^o = -(33479.9 \pm 1.2)\ \mathrm{J \cdot g^{-1}}$.

The procedure described by Waddington *et al.*[14] for combustion calorimetry of organosulphur compounds was followed. The $RCONHCSNR'_2$ compounds were burned in pellet form under a $p = 3.04$ MPa oxygen atmosphere, and in the presence of 10.0 cm^3 (HFET) or 5.0 cm^3 (HFIB) of water. The amount of nitric acid was determined using Devarda's method. At $T = 298.15$ K, $(\partial u/\partial p)_T$ for these compounds was assumed to be $-0.2\ \mathrm{J \cdot g^{-1} \cdot Pa^{-1}}$, which is a typical value for organic solids.[15] The procedure given by Hubbard *et al.*[16] was used for the calculation of $\Delta_c u^o$.

The standard molar enthalpies of sublimation of both HFET and HFIB were measured using the *vacuum sublimation* drop microcalorimetric method,[17] in which samples (about 3 mg) of each crystalline compound, contained in a thin one-end sealed glass capillary tube are dropped from room temperature to the hot zone of the calorimetric cell and then evacuated. The Calvet microcalorimeter apparatus (SETARAM HT 1000) hot zone was held at $T = 385$ K in both studies. The observed enthalpies of sublimation $\{H^o_m(\mathrm{g}, 385\ K) - H^o_m(\mathrm{cr}, 298\ \mathrm{K})\}$ were corrected to $T = 298.15$ K, by estimating $\Delta^{385\ \mathrm{K}}_{298\ \mathrm{K}} H^o_m(\mathrm{g})$ using a group contribution method based on the Stull *et al.*[18] values. The calibration of this calorimetric system was carried by the sublimation of naphthalene samples, $C_{10}H_8$, $\Delta^g_{cr} H^o_m(C_{10}H_8) = (72.51 \pm 0.01)\ \mathrm{kJ \cdot mol^{-1}}$.[19] The calibration constant was set as $k_{385\ \mathrm{K}} = (18.42 \pm 0.28)\ \mathrm{mJ \cdot V^{-1} \cdot s^{-1}}$ from six independent experiments.

3. Results

Table 1 lists typical combustion experimental results for each compound. In this table, Δm (H_2O) represents the departure from the 4059.0 g of the water added to the calorimeter, the mass of water assigned to ε(calor), ΔU_Σ is the correction to the standard state, and the remaining terms are as previously described.[16] As the final temperature of the main period is $T = 298.15$ K,

TABLE 1. Typical combustion experimental results for *N*,*N*-diethyl-*N*′-furoylthiourea, HFET, and *N*,*N*-diisobutyl-*N*′-furoylthiourea, HFIB, at $T = 298.15$ K

	HFET	HFIB
m(cpd)/g	0.80350	0.68656
m(fuse)/g	0.00408	0.00470
$(T_i/K) - 273.15$	23.8947	23.9122
$(T_f/K) - 273.15$	24.9998	24.9853
ΔT_{ad}/K	1.07214	1.04056
$\varepsilon_i/(J \cdot K^{-1})$	74.70	33.21
$\varepsilon_f/(J \cdot K^{-1})$	74.34	33.11
$\Delta m(H_2O)$/g	+0.4	+2.4
$-\Delta U$(IBP)/J[a]	22263.49	21573.19
$\Delta U(HNO_3)$/J	66.86	47.16
ΔU(ign)/J	1.18	1.19
ΔU_Σ/J	33.89	14.80
$-m\Delta_c u^o$(fuse)/J	66.26	76.33
$-\Delta_c u^o(cpd)/(J \cdot g^{-1})$	27500.2	31220.9

[a] ΔU(IBP) includes ΔU(ign); m(cpd) mass of compound burnt in each experiment; m(fuse) mass of fuse (cotton) used in each experiment; ΔT_{ad} corrected temperature rise/variation of adiabatic temperature; T_i and T_f initial and final temperatures of main period; ε_i, ε_f energy equivalent of contents in the initial and final states; $\Delta m(H_2O)$ deviation of the mass of water added to the calorimeter from 4059.0 g; ΔU(IBP) energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(HNO_3)$ energy correction for the nitric acid formation; ΔU_Σ standard state correction; $m\Delta_c u^o$(fuse) energy of combustion of the cotton fuse; $\Delta_c u^o$(cpd) compound massic energy of combustion.

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(H_2O, l)\Delta m(H_2O)\}\Delta T_{ad} + \varepsilon_i(T_i - 298.15) + \varepsilon_f(298.15 - T_i - \Delta T_{ad}) + \Delta U(\text{ign}),$$

where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and work done due to stirring. Table 2 lists the individual values of $-\Delta_c u^o$ together with its mean and standard deviation. In table 3, the derived standard molar enthalpies of combustion and formation in the crystalline and gaseous states at $T = 298.15$ K are listed. The uncertainties assigned to the standard molar enthalpies of combustion and formation, in accordance with normal thermochemical practice, are taken as twice the overall standard deviation of the

TABLE 2. Individual values of the massic energies of combustion $-\Delta_c u^o$ of N,N-diethyl-N'-furoylthiourea, HFET, and N,N-diisobutyl-N'-furoylthiourea, HFIB, at $T = 298.15$ K

HFET	HFIB
$-\Delta_c u^o/(J \cdot g^{-1})$	
27513.8	31214.4
27487.9	31226.9
27500.2	31218.1
27515.2	31213.2
27494.4	31219.6
27520.8	31220.9
27502.4	
$\langle -\Delta_c u^o \rangle/(J \cdot g^{-1})$	
27505.0 ± 4.5	31218.8 ± 2.0

$\langle -\Delta_c u^o \rangle$ represents the mean values.

TABLE 3. Derived standard ($p^o = 0.1$ MPa) molar energies of combustion, $\Delta_c U^o_m$, standard molar enthalpies of combustion, $\Delta_c H^o_m$, standard molar enthalpies of formation, $\Delta_f H^o_m$ and standard molar enthalpies of sublimation, $\Delta^g_{cr} H^o_m$, at $T = 298.15$ K, for N,N-diethyl-N'-furoylthiourea, HFET, and N,N-diisobutyl-N'-furoylthiourea, HFIB

	$\frac{-\Delta_c U^o_m(cr)}{kJ \cdot mol^{-1}}$	$\frac{-\Delta_c H^o_m(cr)}{kJ \cdot mol^{-1}}$	$\frac{\Delta_f H^o_m(cr)}{kJ \cdot mol^{-1}}$	$\frac{\Delta^g_{cr} H^o_m}{kJ \cdot mol^{-1}}$	$\frac{\Delta_f H^o_m(g)}{kJ \cdot mol^{-1}}$
HFET	6224.4 ± 3.0	6231.8 ± 3.0	-306.1 ± 3.3	132.0 ± 3.5	-174.1 ± 4.8
HFIB	8816.4 ± 3.3	8828.8 ± 3.3	-426.4 ± 3.8	141.7 ± 5.6	-284.7 ± 6.8

mean and include the errors from the calibration and use of auxiliary data. To derive $\Delta_f H^o_m$ from $\Delta_c H^o_m$, the following standard enthalpies of formation, at $T = 298.15$ K, of $H_2O(l)$, $-(285.83 \pm 0.04)$ kJ · mol^{-1} [20] and $CO_2(g)$, $-(393.51 \pm 0.13)$ kJ · mol^{-1} [20] were used.

The individual results of the enthalpies of sublimation of HFET and HFIB are given at table 4, where once again the quoted uncertainties are equal to twice the standard deviation of the mean.

TABLE 4. Individual microcalorimetric standard ($p^o = 0.1$ MPa) molar enthalpies of sublimation $\Delta_{cr}^{g}H_m^o$, at $T = 298.15$ K, for *N*,*N*-diethyl-*N*′-furoylthiourea, HFET, and *N*,*N*-diisobutyl-*N*′-furoylthiourea, HFIB

HFET	HFIB
$\Delta_{cr}^{g}H_m^o(T = 298.15\ \text{K})/(\text{kJ}\cdot\text{mol}^{-1})$	
125.5	132.8
127.6	135.6
129.4	140.6
131.7	142.8
135.5	147.1
136.7	151.1
137.5	
$\langle\Delta_{cr}^{g}H_m^o\rangle^a(T = 298.15\ \text{K})/(\text{kJ}\cdot\text{mol}^{-1})$	
132.0 ± 3.5	141.7 ± 5.6

[a] $\langle\Delta_{cr}^{g}H_m^o\rangle$ represents the mean values.

4. Discussion

Since the compounds in this study are reported for the first time, there are no previous results regarding their thermochemistry or any other physical properties. However, there are a few papers about the thermochemistry of related compounds as benzoylureas[7] and on the additivity of thermodynamic properties of alkylureas.[21,22] As it was previously done for other compounds of the same acylchalcogenoureas family,[7] the self-consistency of the results can be tested from the difference of the enthalpies of formation of the two compounds, which corresponds to the substitution of an ethyl by an *iso*-butyl group. As estimated previously[7] from group energy contributions, this enthalpic difference should correspond to 99.3 $\text{kJ}\cdot\text{mol}^{-1}$. On the other hand, a simple difference between the corresponding standard molar enthalpies of formation in the gaseous phase[23] yields a difference of (108 ± 3) $\text{kJ}\cdot\text{mol}^{-1}$, well in accordance with the experimental difference found for the pair of thioureas reported in this paper, (110 ± 8) $\text{kJ}\cdot\text{mol}^{-1}$.

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WE-295