

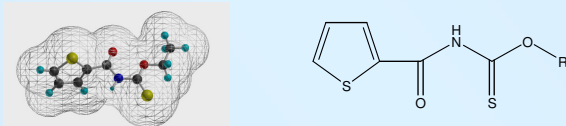
# Thermochemical studies on *N*-thenoylthiocarbamic-*O*-*n*-alkyl esters



AIM

*N*-acylthiocarbamic-*O*-alkylesters had their first appearance as early as 1874 reported by L. Lössner [1] followed by the identification by A. E. Dixon [2] in 1895. For many years, they have been overlooked as chelating ligands in spite of their easy synthetical access. The first reference due to their coordinating properties was published in 1995 [3]. Recently, more attention has been devoted to the thermodynamical properties of these ligand systems [4] as well as their transition metal complexes [5-7].

FIGURE 1. General formula of the *N*-thenoylthiocarbamic-*O*-alkyl esters.



The enthalpies of combustion of five *N*-thenoylthiocarbamic-*O*-*n*-alkyl esters were measured at  $T=298.15\text{K}$  by rotating bomb calorimetry and the standard molar enthalpies of formation were derived. Standard molar enthalpies of sublimation were measured using high temperature Calvet microcalorimetry. The temperatures and enthalpies of fusion were determined for all compounds.

## EXPERIMENTAL

### SYNTHESIS

The *N*-thenoylthiocarbamic-*O*-alkylesters were prepared by adapting the procedure for the synthesis of *N*-benzoylthiocarbamic-*O*-alkylesters as described in reference [3]: 0.1 mol (16.3 g) of thenoyl isothiocyanate were dissolved in 60 cm<sup>3</sup> of toluene; the corresponding alcohol was added dropwise in twofold molar excess at room temperature under stirring and slowly heated up to 333 K for one hour. Over night, the reaction mixture was evaporated to dryness. The remaining crude solid was dissolved in methanol, and water was added up to maintaining turbidness. Continually repeating of this procedure leads to pure, yellow crystals.

### ROTATING BOMB COMBUSTION CALORIMETRY

The energies of combustion of the crystalline *N*-thenoylthiocarbamic-*O*-alkylesters were measured using a rotating bomb calorimeter. The energy equivalent of the calorimeter was chemically determined from the combustion of benzoic acid (Bureau of Analysed Samples - CRM 190r). That equivalent is  $20369.0 \pm 2.3 \text{ J}\cdot\text{K}^{-1}$  for a mass of 3965.0 g of water.

### SUBLIMATION ENTHALPIES BY CALVET MICROCALORIMETRY

The enthalpies of sublimation were measured using the "vacuum sublimation" drop-microcalorimetric method. [8-9]

The observed enthalpies of sublimation  $\{H(g, T) - H(cr, 298.15 \text{ K})\}$  were corrected to  $T=298.15 \text{ K}$  using estimated  $\{H(g, T) - H(g, 298.15 \text{ K})\}$  values calculated from the harmonic vibrational frequencies at the B3LYP/6-311++G(d,p) applying a scale factor of 0.9613.

The calorimeter was calibrated *in situ*, making use of the reported enthalpy of sublimation of naphthalene ( $72.600 \pm 0.600$ ) kJ·mol<sup>-1</sup>. [10]

### DIFFERENTIAL SCANNING CALORIMETRY

To measure the temperatures and enthalpies of fusion for all compounds, a heat power compensation d.s.c. type, model Setaram DSC-141, was employed at a heating rate of 0.0833 K·s<sup>-1</sup>. The crucibles containing the sample and the empty crucibles used as the reference were made of aluminium and had a volume of 30 mm<sup>3</sup>. The temperature and heat flux scales were calibrated by measuring the fusion of In and at the same heating rate. Measurements of the temperature of fusion and of the enthalpy of fusion of benzoic acid (NIST SRC 39i) were made in our laboratory to verify the accuracy of the instrument.

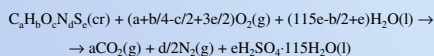
### COMPUTATIONAL THERMOCHEMISTRY

For all involved species, full geometry optimizations with Becke's three-parameter exchange functional [11] in combination with the Lee, Yang and Parr correlation function as hybrid exchange-correlation energy functional (B3LYP) [12] at a 6-311++G(d,p)-level of theory, were performed, to yield the most stable geometries. The zero-point energies (εZPE) are scaled to 0.9804 [13]. Harmonic vibrational frequencies were calculated at the same level of theory, applying a scaling factor 0.9613 for the correction of anharmonicity [13], using the implementation of DFT in the Gaussian03 suite of programs [14].

## RESULTS

### ROTATING BOMB COMBUSTION CALORIMETRY

The standard massic energy of combustion,  $\Delta_c u^0$ , was calculated following the procedure from Hubbard *et al.*, accordingly to the idealised reaction, represented by:



The standard molar enthalpies of combustion as well as sublimation, and the standard molar enthalpies of formation, in the crystalline and the gaseous phases, all of them with their respective uncertainties, are presented in table 1.

The calculations of the standard molar enthalpies of formation are based on the literature values [15].

ACKNOWLEDGEMENTS: Thanks are due to:

- Fundação para a Ciência e Tecnologia (FCT) and by the Programa Operacional Ciência e Inovação 2010 (POCI 2010) for the financial support of the project ref: POCI/QUI/61873/2004.
- Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química, University of Porto. Bernd Schröder is grateful to FCT and the European Social Fund (ESF) under the 3rd Community Support Framework (CSF) for the award of a Post-Doc scholarship (BPD 35131/2000).

Bernd Schröder, Isabel M. M. Monteiro, Luís M. N. B. F. Santos, and Manuel A. V. Ribeiro da Silva

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal



Table 1

Derived standard ( $p^0 = 0.1 \text{ MPa}$ ) molar enthalpies of combustion  $\Delta_c H_m^0$ , standard molar enthalpies of sublimation,  $\Delta_g^0 H_m^0$ ,  $298.15 \text{ K}$ , and standard molar enthalpies of formation  $\Delta_f H_m^0$  in the solid and gaseous state, at  $T = 298.15 \text{ K}$ .

|         | $-\Delta_c H_m^0(\text{cr}) / \text{kJ}\cdot\text{mol}^{-1}$ | $-\Delta_f H_m^0(\text{cr}) / \text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_g^0 H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$ | $-\Delta_f H_m^0(\text{g}) / \text{kJ}\cdot\text{mol}^{-1}$ |
|---------|--|--|--|---|
| Httcc   | $5312.8 \pm 3.1$   | $325.5 \pm 3.3$  | $143.2 \pm 3.1$                                    | $182.3 \pm 4.5$   |
| Httpe   | $5990.8 \pm 2.5$   | $326.8 \pm 2.8$  | $136.5 \pm 1.8$                                    | $190.3 \pm 3.3$   |
| Htuba   | $6648.5 \pm 2.5$   | $348.4 \pm 2.9$  | $147.5 \pm 1.9$                                    | $200.9 \pm 3.5$   |
| Httpepe | $7297.6 \pm 3.8$   | $378.7 \pm 4.0$  | $165.6 \pm 2.1$                                    | $213.1 \pm 4.5$   |
| Htuba   | $7951.9 \pm 3.8$   | $403.8 \pm 4.2$  | $180.1 \pm 3.0$                                    | $223.7 \pm 5.2$   |

Results of the d.s.c. measurements of fusion temperatures and standard molar enthalpies of fusion, as well as the derived standard molar entropies of fusion, for all *N*-thenoylthiocarbamic-*O*-alkyl esters, are listed in table 2. The error associated to the temperatures of fusion is based on the estimate of error of the temperature calibration.

Table 2

Fusion temperatures, standard molar enthalpies of fusion and standard molar entropies of fusion of *N*-thenoylthiocarbamic-*O*-alkylester.

| Compound | $T_{\text{melt}} / \text{K}$ | $\Delta_c H_m^0(T_{\text{melt}}) / \text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_c S_m^0(T_{\text{melt}}) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ |
|----------|------------------------------|---|--|
| Httcc    | 345.9                        | $21.90 \pm 0.43$  | $63.3 \pm 1.2$   |
| Httpe    | 370.1                        | $26.10 \pm 0.46$  | $70.5 \pm 1.2$   |
| Htuba    | 364.3                        | $23.89 \pm 0.39$  | $65.6 \pm 1.1$   |
| Httpepe  | 354.3                        | $24.59 \pm 0.44$  | $69.4 \pm 1.2$   |
| Htuba    | 346.4                        | $22.48 \pm 0.37$  | $64.9 \pm 1.1$   |

In figure 2, the entropies of fusion at fusion temperature are presented as a function of the carbon number (CN) in the alkyl group. The entropies of fusion show a distinctive odd (Httpe, Httpepe) and even (Htuba, Httcc) effect, subjected to the number of carbon atoms (CN) in the ester group. The odd effect indicates less entropy in the solid state and therefore a higher degree of order in the crystal structure than in the even counterparts.

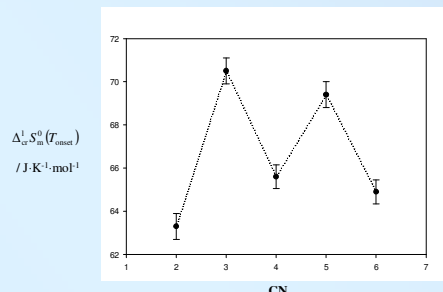


Figure 2. Plot of the standard molar entropies of fusion at individual fusion temperatures vs. the number of carbon atoms (CN) of the alkyl chain for the studied *N*-thenoylthiocarbamic-*O*-alkyl esters.

### FINAL REMARKS

Linear regression gives  $\Delta_f H_m^0(\text{g}) = -(10.6 \pm 0.8) \cdot \text{CN} - (159.8 \pm 3.4)$  ( $R^2 = 0.9956$ ) with CN as the number of carbon atoms in the alkyl rest (CN>1). The slope of  $-10.6 \text{ kJ}\cdot\text{mol}^{-1}$  as the increment in the standard molar enthalpy of formation in the gaseous state due to succeeding CH<sub>2</sub>-group introduction in the alkyl chain is significantly lower than expected by the Allen scheme, which suggests a group energy contribution of [C-(C)(H)2] =  $-20.5 \text{ kJ}\cdot\text{mol}^{-1}$ . This increment is also slightly lower than the one found for *N*-benzoylthiocarbamic-*O*-alkyl esters ( $-14.8 \text{ kJ}\cdot\text{mol}^{-1}$ ), with linear regression coefficients  $\Delta_f H_m^0(\text{g}) = -(14.8 \pm 0.9) \cdot \text{CN} - (183.2 \pm 3.8)$  ( $R^2 = 0.9991$ ) [4].

DFT calculations with the B3LYP functional at a 6-311++G(d,p)-level of theory resulted in an excellent correlation of the calculated energies with the number of carbon atoms (CN) in the ester group, both *N*-thenoylthiocarbamic-*O*-alkyl esters and in *N*-benzoylthiocarbamic-*O*-alkyl esters, as well as for the related alkanes. The found slopes of these correlations indicate the same tendency as found in the experimental results, concerning the magnitude of difference in the [C-(C)(H)2] increment.

### REFERENCES

- L. Lössner, *J. Prakt. Chem.* 10 (1874) 258-261.
- A. E. Dixon, *J. Chem. Soc.* 97 (1895) 1048-1049.
- U. Schröder, L. Beyer, F. Dietze, R. Richter, S. Schmidt, E. Hoyer, *J. Prakt. Chem.* 237 (1995) 184-188.
- M. A. V. Ribeiro da Silva, L. M. N. B. F. Santos, B. Schröder, L. Beyer, *J. Chem. Thermodyn.* 36 (2004) 491-498.
- L. Dias, U. Schröder, B. Schröder, F. Dietze, L. Beyer, *Solv. Extr. Ion. Exch.* 18 (2000) 1617-1177.
- B. Schröder, U. Schröder, F. Dietze, L. Beyer, *Inorg. Chem. Comm.* 4 (2001) 398-401.
- M. A. V. Ribeiro da Silva, L. M. N. B. F. Santos, B. Schröder, L. Beyer, *J. Chem. Thermodyn.* 36 (2004) 427-431.
- F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade, R. A. Skinner, *J. Organometallic Chem.* 97 (1975) 221-228.
- L. M. N. B. F. Santos, B. Schröder, O. P. Fernandes, M. A. V. Ribeiro da Silva, *Thermochimica Acta* 415 (2004) 15-20.
- R. Sabido, A. Xu, J. S. Chiketa, M. L. F. Lima, L. M. V. R. Lima, L. A. Torres, *Thermochimica Acta* 331 (1999) 93-204.
- A. D. Becke, *Phys. Rev. A: At. Mol. Opt. Phys.* 38 (1988) 3098-3100.
- A. D. Becke, *J. Chem. Phys.* 98 (1993) 6468-6472.
- M. W. Wong, *Chem. Phys. Letters* 256 (1996) 391-399.
- Gaussian 03, Revision A.1.
- CODATA, *J. Chem. Thermodyn.* 10 (1978) 903.