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Measurement and prediction of enthalpies of combustion and formation of oxygen and nitrogen heterocycles

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Abstract

Enthalpies of combustion and formation are reported for six *O*-heterocyclic and four *N*-heterocyclic compounds in crystalline or liquid phases. By the use of estimated enthalpies of fusion and vaporisation, liquid and gas enthalpies of formation were derived and compared with values predicted directly by the NIST Structures and Properties program and by the Pedley method. The results are discussed in relation to ring strain energies and the strength and weaknesses of the predictive methods are compared. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Enthalpies of combustion; Enthalpies of formation; Oxygen heterocycles; Nitrogen heterocycles; Ring strain energies

1. Introduction

Industrial thermodynamic data requirements, for route selection, process development and determination of safe operating conditions, are provided by a combination of literature sources, predictive methods and in house measurement. Prediction methods are increasingly important and are frequently used in conjunction with theoretical models, but their reliability is variable. The development of these methods is dependent upon availability of data for molecules with a sufficient range of functional group interactions, but a large proportion of literature data relate to relatively simple molecules or to only one member of a series, thus preventing the derivation of constant group contribution parameters that fully reflect the group interactions. There are notable exceptions to this, including

recent work at the Universities of Manchester and Porto, e.g. [1,2] but the relative lack of data on polyfunctional molecules has limited the ability to predict their properties without simplifying assumptions. This applies particularly to heterocyclic compounds in which ring strain energy is a complicating factor.

A further aspect of industrial thermodynamics is the importance of relating the accuracy and precision to the requirements of the application. It may be quite sufficient to know the enthalpy of reaction to within $\pm 25 \text{ kJ mol}^{-1}$ for certain purposes, for example the design of a cooling system, whereas much greater precision is required for equilibria calculations. It is therefore more important to know the reliability or accuracy of a result and its uncertainty than to have a precise value. A predictive method is therefore valuable if it offers such a value, even with an uncertainty much greater than would be acceptable for theoretical thermodynamic purposes.

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The purpose of this paper is (i) to report enthalpies of combustion and formation of a number of substituted *O*- and *N*-heterocyclic compounds determined over a number of years, and (ii) to compare the results with values predicted by the NIST Structures and Properties method [3] and the more complex Pedley method [4]. It is a common experience in industrial applications to find an enthalpy of formation is required for a solid or liquid state but that a predicted value can be obtained only for the gas or liquid state and, in the absence of known vaporisation or sublimation enthalpies, resort must again be made to predictive methods for these properties. While not of a standard suitable for rigorous thermodynamic purposes, the results can nevertheless offer good levels of accuracy that are sufficient for the purpose. This same approach has been adopted in the comparisons discussed in this paper.

The two $\Delta_f H^0$ estimation methods used differ considerably. The NIST S and P program is based on the Benson group contribution method and includes a database of ca. 5000 compounds. It offers easy input of structure, is searchable by name, formula or structure, can estimate $\Delta_f H^0$, S and C_p and is available for PC use. It has the disadvantage however, that only gas phase values can be estimated and it fails with compounds containing groups for which fragment values are not known. Some ring corrections are also missing and no guidance is given on the uncertainty of the estimate.

The Pedley method is based on a novel parameterisation of liquid and gas values including, for some compounds, 5-centre interactions, and has a database of >3000 compounds. It is searchable by formula or “attribute” — combinations of functional groups — and offers the important advantage of predicting both liquid and gas values of $\Delta_f H^0$, S and C_p . It suffers from the disadvantages, however, of more complex structure input method and having no non-aromatic ring corrections. Many of these have, however, been tabulated but must be added manually.

2. Experimental

2.1. Materials

Samples were produced in research laboratories within the Company and purified by distillation or

recrystallisation to narrow boiling or melting ranges specifically for the combustion work. The *O*-heterocycles studied were: trimethylene oxide (TMO), 3,3-dimethyloxacyclobutane (3,3-DMOCB), 6,6-dimethyl-1,5,7-trioxaspiro[3.3]nonane (6,6-DMTO), tetramethyl glycolide (TMG), 4-hydroxytetrahydropyran (4-HTHP) and 3,4-dihydro-2H-pyran-2-carbaldehyde (3,4-DHPC). The *N*-heterocycles were: 2-pyrrolidone (2-Pyr), ϵ -Caprolactam (ϵ -Cap), phthalimide (PI) and *N,N*-diphenyl uretidione (*N,N*-DPU). The structures are shown in Table 5.

2.2. Apparatus and procedure

The energies of combustion were measured using an isoperibol static bomb calorimeter: the bomb, constructed of stainless steel, had an internal volume of 0.24 dm³. The energy equivalent of the bomb and the surrounding nickel-plated copper calorimeter can were determined at intervals during the course of this work by combustion of benzoic acid (NBS Thermochemical Standard, 39 g). A different bomb (of similar design) was used for 3,4-DHPC and *N,N*-DPU. The energy equivalent of the calorimetric systems was corrected for each experiment for the small variation in the mass of water added to the calorimeter.

Samples for combustion were prepared by forming pellets of mass ca. 1 g of the solid materials or by sealing ca. 1 g liquid in glass ampoules. The samples were placed in a platinum crucible and assembled in the bomb with a fuse of platinum wire coiled around a 10 mm length of cotton thread. The energy equivalent of the thread was previously determined as $\Delta_c u = 900 \text{ J m}^{-1}$. A small amount of petroleum jelly, $\Delta_c u = -46190 \text{ J g}^{-1}$, was often added to the ampoules as a fuse aid. A 1 cm³ volume of water was added to the bomb, which was then sealed, pressure tested and purged with oxygen. The bomb was then charged with oxygen to a pressure $p = 3.04 \text{ MPa}$ and assembled in the calorimeter can, which was fitted with a stirrer, internal heater and lid. A measured quantity of water was added to the can to just cover the bomb. Combustions of 2-Pyr were unsuccessful using only a small amount of petroleum jelly; successful combustions were achieved by coating the ampoules with a larger quantity.

The combustions were carried out with the calorimeter located within an air jacket in a thermostat bath controlled to ± 0.002 K. The temperature of the bomb was measured by a long stem 25 ohm platinum resistance thermometer. Combustions were initiated at temperature in the range 298.15 ± 0.50 K. The electrical ignition energy dissipated in the platinum fuse was measured directly for each combustion.

The reaction products were analysed for CO by passing the product gases through a Draeger tube and the bomb examined for evidence of unburnt carbon; in either case if more than a slight trace was present the run was discarded. It was otherwise assumed that all the sample was fully combusted. The presence of HNO_3 in the product solution was determined where appropriate by titration with NaOH; the correction was based on $-59.7 \text{ kJ mol}^{-1}$ for the energy of formation of 0.1 mol dm^{-3} HNO_3 from N_2 , O_2 and $\text{H}_2\text{O}(l)$ [5].

3. Results

Temperature readings were taken at 15 s intervals before and after the ignition. Smooth curves were fitted to the pre- and after-period temperatures and the corrected temperature rise was calculated by the Dickinson method, in which ΔT_{corr} is the ordinate that encloses equal areas above and below the reaction curve [6]. Typical sets of results for the combustion of each compound are given in Table 1. The energy equivalent ($\varepsilon_{\text{cal}} + \varepsilon_f$) is that of the calorimeter system plus the combustion products.

As samples were ignited near $T = 298.15$ K, then $\Delta U(\text{IBP}) = -\{\varepsilon_{\text{cal}} + \varepsilon_f\}\Delta T_{\text{corr}} + \Delta U_{\text{ign}}$. The terms in Table 1 are as previously described [6] with ΔU_{Σ} being the correction to the standard state.

The individual values of $\Delta_c H_m^0$ for each combustion are listed in Tables 2–4 together with the mean and the overall uncertainty of twice the standard deviation of the mean, including the uncertainties in calibration. Molar enthalpies of formation $\Delta_f H_m^0$ were derived using literature values [5] of

$$\Delta_f H_m^0(\text{H}_2\text{O}, l) = -285.83 \pm 0.04 \text{ kJ mol}^{-1} \text{ and}$$

$$\Delta_f H_m^0(\text{CO}_2, g) = -393.51 \pm 0.13 \text{ kJ mol}^{-1}.$$

4. Discussion

To compare the experimental $\Delta_f H_m^0$ results with predicted values it was necessary to derive gas phase, and in some instances liquid phase, values from the experimental results. This should normally be carried out calorimetrically or by derivation of $\Delta_1^g H_m^0$ from vapour pressure measurements. These values were not required for the original purpose of the work and therefore were not available. To allow the comparisons to be made, for the reasons outlined earlier, values of $\Delta_1^g H_m^0$ were determined by the methods described by Klein–Fishtine, Riedel, Chen and Guaiacolone [7]. These in turn require knowledge of the critical properties T_c and P_c ; they were not known for any of the compounds in question and were therefore estimated by the Joback method [8]. The mean accuracy of the Joback method is stated as ± 4.8 K for over 400 organic compounds [9], and that of the $\Delta_1^g H_m^0$ methods as ca. $\pm 2\%$. The accuracies are recognised to vary with the compound type and no formal attempt was made to quantify their suitability for these compounds.

As there are no satisfactory generally applicable methods for prediction of $\Delta_{\text{cr}}^1 H_m^0$, a value of 125 J g^{-1} was arbitrarily taken unless a literature value was known, based on very many organic compounds having $\Delta_{\text{cr}}^1 H_m^0$ values in the range $125 \pm 30 \text{ J g}^{-1}$. Whilst not the ideal approach, the variation of $\Delta_{\text{cr}}^1 H_m^0$ between molecules is substantially less than that of $\Delta_1^g H_m^0$ and therefore introduces less uncertainty into the estimate of $\Delta_f H_m^0(g)$.

The values thus arrived at are listed in Table 5 under the column headed “Experimental” to indicate their derivation from the experimental measurements. For clarity, however, they are indicated as “E”, to differentiate from the solid or liquid phase results derived from the experimental data without any recourse to estimation of transition enthalpies. The liquid and gas phase $\Delta_f H_m^0$ values predicted by the Pedley method and the gas phase values from S and P are tabulated opposite the corresponding values, together with the differences $\delta = (\Delta_f H_m^0(\text{exp}) - \Delta_f H_m^0(\text{pred}))$.

In a few instances, literature values are known and are shown in the Experimental column for comparison. The literature $\Delta_f H_m^0(g)$ value for TMO agrees very closely with the experimentally derived value of $-80.2 \text{ kJ mol}^{-1}$ in this work. There is also good agreement between the experimental and literature

Table 1
Typical experimental data^a

	TMO	3,3-DMOCB	6,6-DMTO	TMG	4-HTHP	3,4-DHPC	2-Pyr	ϵ -Cap	PI	<i>N,N</i> -DPU
<i>m</i> (cpd) (g)	1.07812	1.06814	1.67226	1.70330	0.97633	0.84035	1.37378	1.21673	1.27366	1.33616
<i>m</i> (fuse aid) (g)	0.03049	0.01688	–	–	0.02088	0.01458	0.10541	–	0.01181	–
ΔT_{corr} (K)	2.1160	2.3025	2.7788	2.2560	1.6401	1.5135	2.4046	2.2077	1.7497	2.0167
$(\epsilon_{\text{cal}} + \epsilon_r)/J\text{ K}^{-1}$	17577.3	17630.3	17591.8	17599.8	17525.3	19116.8	17575.1	17606.1	17913.6	2.0167
$-\Delta U(\text{IBP})$ (J)	37173.0	40577.0	48862.7	39681.1	28726.4	28915.8	4223.70	38847.6	31328.9	38268.7
$\Delta U(\text{HNO}_3)$ (J)	0.0	0.0	0.0	0.0	0.0	0.0	86.9	69.4	55.7	56.8
$\Delta U(\text{ign.})$ (J)	20.6	16.8	21.4	24.0	16.8	17.5	24.1	21.4	14.4	16.5
ΔU_{Σ} (J)	14.5	15.6	26.5	27.7	12.8	19.3	19.6	22.3	21.6	34.6
$-\Delta U(\text{fuse aid})$ (J)	1408.33	779.7	–	–	964.5	673.5	4868.9	–	545.5	–
$-\Delta_c u^0(\text{cpd})$ (J g^{-1})	33151.4	37235.5	29198.3	23275.1	28412.6	33574.1	27116.9	31845.2	24101.5	28565.7
$-\Delta_c H_m^0$ (cpd) (kJ mol^{-1})	1927.9	3212.2	4624.0	4010.0	2905.6	3229.9	2309.7	3609.7	3544.9	6806.9

^aFor all experiments, ΔU (cotton fuse) = 9.0 J.

Table 2

Summary of standard molar enthalpies of combustion, $-\Delta_c H_m^0$ (kJ mol⁻¹) — O-heterocyclic compounds

TMO	3,3-DMOCB	6,6-DMTO	TMG	4-HTHP	3,4-DHPC
1928.9	3212.2	4624.2	4009.8	2906.4	3232.2
1926.9	3213.7	4622.2	4010.0	2909.0	3224.6
1927.9	3210.5	4624.0	4010.0	2905.6	3229.9
			4008.4	2904.0	3233.6
					3227.5
1927.9 ± 1.3	3212.1 ± 2.0	4623.5 ± 1.8	4009.6 ± 1.3	2906.3 ± 2.2	3229.6 ± 3.4

[11] results for 2-Pyr (I); the Pedley predicted value agrees moderately well but is rather closer to an earlier literature value of $\Delta_f H_m^0 = -286.2$ kJ mol⁻¹ [13], while the experimentally derived gas phase value is close to the predicted value. There is some uncertainty around the enthalpy of vaporisation.

The experimental result for ϵ -Cap (cr) agrees very closely with literature, and the Pedley predicted gas phase value is very close to the derived gas value. It is therefore surprising that the experimental and predicted liquid values agrees less well.

The experimental $\Delta_f H_m^0$ (cr) = -318.2 ± 2.1 kJ mol⁻¹ for PI is not very different from the value listed by Kharasch [12] with the qualification that its reliability was unknown. It is therefore surprising that the predicted liquid and gas values differ substantially from the experimentally derived values.

The overall level of agreement between experimental and predicted values is generally better than ± 20 kJ mol⁻¹ for the O-heterocycles, which is sufficient for many industrial purposes. The differences are much more variable however, for N-heterocycles.

Table 3

Summary of standard molar enthalpies of combustion, $-\Delta_c H_m^0$ (kJ mol⁻¹) — N-heterocyclic compounds

2-Pyr	ϵ -Cap	PI	N,N-DPU
2316.8	3607.9	3541.1	6807.0
2306.7	3612.3	3544.4	6799.4
2312.2	3605.7	3547.1	6806.6
2309.7	3606.3	3545.0	6806.9
2302.9	3606.5	3544.9	6810.1
2303.0			
2308.5 ± 4.5	3607.7 ± 2.6	3544.5 ± 2.1	6806.0 ± 4.1

The results for TMO, 3,3-DMOCB and 6,6-MTO suggest the ring strain in the trimethylene oxide ring does not differ greatly between the compounds, despite the differences in substitution. TMG, however, is evidently less stable than predicted, suggesting greater steric interaction between the dimethyl groups and adjacent carbonyl groups. There is a surprising and unaccountable discrepancy between experimental and predicted values for 4-HTHP; in view of the close agreement between Pedley, and S and P the possibility of an erroneous experimental result has to be considered.

Results for the N-heterocycles are less consistent. While the gas phase Pedley values for the two lactones agree well with the experimental results, the liquid phase results show moderate discrepancies, the rings apparently being stabilised less than predicted. The diketone rings, however, are substantially less stable than predicted in both liquid and gas phase. It is apparent there are problems in the derivation and prediction of ring strain energies for keto-substituted N-heterocycles, particularly for less than 6-membered rings.

Table 4

Derived molar values at $T = 298.15$ K, $p = 0.1$ MPa

	State	$\Delta_f H_m^0$ (kJ mol ⁻¹)
TMO	l	-110.2 ± 1.3
3,3-DMOCB	l	-184.6 ± 2.0
6,6-DMTO	l	-525.4 ± 1.8
TMG	cr	-853.5 ± 1.3
4,4-HTHP	l	-490.4 ± 2.2
3,4-DHPC	l	-274.8 ± 3.4
2-Pyr	l	-265.9 ± 4.5
ϵ -Cap	cr	-325.5 ± 2.6
PI	cr	-318.2 ± 2.1
N,N-DPU	cr	-132.3 ± 4.1

Table 5
Comparison of experimental and predicted $\Delta_f H_m^0$ values (kJ mol^{-1})



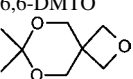
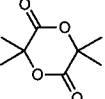




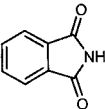
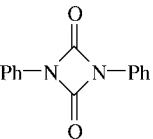
Compound	State	Experimental	Pedley		S and P	
			Pred	δ	Pred	δ
 TMO	l	-110.2 ± 1.3	- 101.0	-9.1		
	g	-80.2 (E)	-77.8	- 2.4	- 77.8	- 2.4
	g	-80.5 [10]				
 3,3-DMOCB	l	-184.6 ± 2.0	- 169.8	- 14.8		
	g	-151.1 (E)	-141.1	- 10.0	-140.4	- 10.7
 6,6-DMTO	l	-525.4 ± 1.8	- 515.1	- 10.3		
	g	-467.6 (E)	- 464.8	-2.8	- 587.4 ^a	
 TMG	cr	-853.5 ± 1.3				
	l	-831.9 (E)	- 844.1	12.2		
	g	-753.7 (E)	- 785.2	31.5	- 879.0 ^a	
 4-HTHP	l	-490.4 ± 2.2	- 448.3	- 42.1	- 837.5 ^b	83.8 ^b
	g	-426.3 (E)	- 389.1	- 37.2	- 392.4	- 33.9
 3,4-DHPC	l	-274.8 ± 4.5	-290.4	15.6		
	g	-225.2 (E)	-243.1	17.9	- 242.9	17.7
 2-Pyr	l	-265.9 ± 4.5	- 281.8	15.9		
	g	-217.3 (E)	- 222.2	4.9	- ^c	-
 ε-Cap	cr	-324.4 ± 2.6				
	cr	-329.4 ± 0.9 [13]				
	l	-311.6	- 331.4	19.8		
 PI	g	-254.9	- 255.5	0.6	- ^c	-
	cr	-318.2 ± 2.1				
	cr	-305.4 [12]				
	l	-299.7	- 358.7	59.9		
	g	-211.4	- 259.1	47.7		

Table 5 (Continued)

Compound	State	Experimental	Pedley		S and P	
			Pred	δ	Pred	δ
N,N-DPU	cr	-132.3 ± 4.1				
	l	-102.4	-160.8	58.4		
	g	+20.7	-13.9	34.6	-	-

^a No ring correction.

^b After applying ring correction ex-Pedley data.

^c No predicted value, but a literature value given.

Comparison of the Pedley and S and P results shows there is generally good agreement on gas phase predicted values; this is encouraging, as the methods are quite independent. Both achieve moderate to good agreement with experimental results for *O*-heterocycles with the exception of 4-HTHP as discussed above. The S and P method suffers from the potentially serious drawbacks, however, that in two instances it predicted values with a warning that ring strain corrections were excluded and without any guidance on the correction, and for the four N-compounds it was unable to predict a value because of missing groups. The S and P method is therefore more likely to fail for a significant proportion of complex heterocyclic compounds. It is clear that in both methods the key to reliable prediction is knowledge of the relevant ring strain energy.

It is concluded that the reliability of prediction of $\Delta_f H_m^0$ values of polyfunctional heterocyclic compounds is very variable and must be undertaken with considerable care. Appraisal of similar compounds is recommended where possible. Neither of the methods used in this work is clearly superior to the other; each has distinct advantages and disadvantages but it is clearly desirable to use two independent methods to provide some degree of corroboration.

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