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STANDARD MOLAR ENTHALPIES OF FORMATION AND SUBLIMATION OF *N*-PHENYLPHTHALIMIDE

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The standard (p^0=0.1 MPa) molar enthalpy of formation, $\Delta_f H_m^0$, for crystalline *N*-phenylphthalimide was derived from its standard molar enthalpy of combustion, in oxygen, at the temperature 298.15 K, measured by static bomb-combustion calorimetry, as –206.0±3.4 kJ mol^{-1}. The standard molar enthalpy of sublimation, $\Delta_{cr}^{g} H_m^0$, at T=298.15 K, was derived, from high temperature Calvet microcalorimetry, as 121.3±1.0 kJ mol^{-1}.

The derived standard molar enthalpy of formation, in the gaseous state, is analysed in terms of enthalpic increments and interpreted in terms of molecular structure.

Keywords: *Calvet microcalorimetry, combustion calorimetry, N-phenylphthalimide, standard molar enthalpy of formation, standard molar enthalpy of sublimation*

Introduction

As a part of our interest on the thermochemistry of nitrogen heterocycle compounds, the substituted phthalimides have recently attracted our attention [1]. Phthalimides, which are bicyclic non-aromatic nitrogen heterocycles, are important compounds with a variety of applications and a wide range of properties. Generally, they are used as starting materials and intermediates for the synthesis of many types of alkaloids and pharmacophores [2], in polymers [3] and copolymers [4], synthesis of pesticides [5] and lately are being under intense biomedical research [6–8] due to their important biological effects. In particular, the *N*-phenylphthalimide besides being used in several herbicides, in reactions with dry ozone, moist ozone and ozone plus ultraviolet light, to simulate certain aspects of the space environment [9], they show hypolipidemic activity lowering the serum cholesterol and triglyceride levels [10], they are dipeptidyl peptidase-IV specific inhibitors [11], have anti-inflammatory activity [12], etc.

Despite their high importance, the thermochemical data on the phthalimides is still limited to only phthalimide [1, 13–15], *N*-methylphthalimide [16, 17], *N*-ethylphthalimide [1] and *N*-propylphthalimide [1].

The present work reports the experimental results of thermochemical studies of *N*-phenylphthalimide [CAS 520-03-06], whose structural formula is represented in Fig. 1.

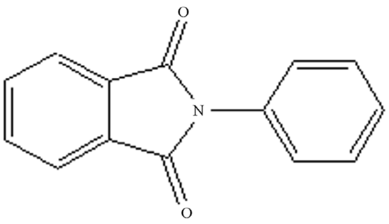

Fig. 1 Structural formula for *N*-phenylphthalimide

The standard (p^0=0.1 MPa) molar enthalpy of combustion, $\Delta_c H_m^0$, in oxygen, at T=298.15 K, was determined by static-bomb combustion calorimetry and the standard molar enthalpy of sublimation, $\Delta_{cr}^{g} H_m^0$, at the same temperature, was obtained from high temperature Calvet microcalorimetric measurements. The derived standard molar enthalpy of formation, in the gaseous state, is analysed in terms of the enthalpic increment due to the introduction of the phenyl group in the phthalimide structure.

Experimental

Materials

Compound and purity control

The *N*-phenylphthalimide was obtained commercially from Aldrich Chemical Co., with the label massic purity of 99.1%. The sample was purified by repeated sublimation under reduced pressure. The purity of the sample was checked by DSC using the fractional fusion technique [18]. A differential scanning calorime-

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ter, Setaram DSC 141, was used. The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high purity reference materials: naphthalene (Aldrich 99.9%), benzoic acid (NIST Standard Reference Material 39i) and indium (Aldrich, mass fraction >0.99999) [19], and the power scale was calibrated with the high purity indium sample as reference material [19]. Curves of samples hermetically sealed in stainless steel crucibles were recorded in an air atmosphere. The crucibles and the samples of compound were weighed on a Mettler UMT2 microbalance with a sensitivity of $1\cdot10^{-6}$ g. For the experimental determinations, samples weighing ≈6 mg were scanned in the temperature from T=298 K to about 15 K above of the melting point, using a heating rate of $8.3\cdot10^{-2}$ K s^{-1}. The recorded curves did not show any phase transitions between T=298 K and the melting temperature of the samples. The onset melting point of *N*-phenylphthalimide was determined as T=484.8 K; literature values: T=476.6–480 K [20] and T=477–480 K [21]. The analyses of the carbon dioxide recovered from the combustion experiments was a supplementary check of the purity of the sample since the average ratio of the mass of carbon dioxide recovered, from eight independent combustion experiments, to that calculated from the mass of sample was: (0.9983±0.0006), where the uncertainty is twice the standard deviation of the mean.

Methods

Combustion calorimetry

The combustion experiments were performed with an isoperibol calorimetric system, with a static bomb (Parr instrument, model 1105); apparatus and procedure have been described [22, 23]. Combustion of certificated benzoic acid BCS-CRM 190p was used for calibration of the bomb. Its specific energy of combustion is –26435.1±3.5 J g^{-1}, under certificate conditions. The calibration results were corrected to give the energy equivalent, ε(calor), corresponding to the average mass of water added to the calorimeter: 3116.3 g. From eighteen independent calibration experiments, ε(calor)=15908.7±1.3 J K^{-1}, where the uncertainty quoted is the standard deviation of the mean. For all experiments, ignition was made at T= 298.150±0.001 K. Samples, in pellet form, were ignited in oxygen, at a pressure p=3.04 MPa, with a volume of 1.00 cm^3 of water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^0$=16250 J g^{-1} [24], a value that has been confirmed in our Laboratory. The corrections for nitric acid formation were based on –59.7 kJ mol^{-1} [25], for the molar energy of formation of 0.1 mol dm^{-3} $HNO_3(aq)$ from N_2, O_2, and $H_2O(l)$. Corrections for the carbon residue soot formation were based on $\Delta_c u^0$= –33 kJ g^{-1} [26].

The amount of *N*-phenylphthalimide used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse. All the necessary weighing was made in a Mettler Toledo AT201 microbalance, sensitivity $\pm1\cdot10^{-6}$ g, and corrections from apparent mass to true mass were made. The average ratio of mass of carbon dioxide recovered after combustions to that calculated from the mass of the samples was 0.9983±0.0006, where the uncertainty is twice the standard deviation of the mean. The density, at T=298.15 K, for *N*-phenylphthalimide is 1.075 g cm^{-3}. The pressure coefficient of massic energy, at T=298.15 K, has been estimated as $(\partial u/\partial p)_T$ = –0.2 J g^{-1} MPa^{-1}, a typical value for most organic compounds [27].

Calorimeter temperatures were measured within the bounds of $\pm1\cdot10^{-4}$ K, at time intervals of 10 s, using a Hewlett-Packard (HP-2804A) quartz crystal thermometer interfaced to an Olivetti M 250E microcomputer programmed to compute the adiabatic temperature change. At least 100 readings were taken for both the fore and after periods, whereas in the main period the number of readings was about 120. Data acquisition and control of the calorimeter was performed by means of the LABTERMO program [28].

For each compound, the massic energy of combustion, $\Delta_c u^0$, was calculated by the procedure given by Hubbard *et al.* [26].

The atomic masses used for the elements were those recommended by the IUPAC in 2001 [29], yielding the molar mass of *N*-phenylphthalimide 223.228 g mol^{-1}.

High temperature microcalorimetry

The standard molar enthalpy of sublimation of *N*-phenylphthalimide was measured using the ‘vacuum sublimation’ drop-microcalorimetric technique, established by Skinner *et al.* [30, 31]. The measurements were performed with a Calvet high-temperature microcalorimeter (Setaram HT 1000) with the vacuum promoted by a rotary vacuum pump and a vapour diffusion pump. Samples of about 3–5 mg of crystalline *N*-phenylphthalimide, contained in small thin glass capillary tubes sealed at one end, and a blank capillary, were simultaneously dropped at room temperature into the hot reaction vessel in the Calvet high-temperature microcalorimeter, held at T=457 K, and then removed from the hot zone by vacuum sublimation. The samples of compound and the glass capillary tubes were weighed on a Mettler CH-8608 analytical balance, with a sensitivity of $1\cdot10^{-6}$ g. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within ±10 μg, into each of the twin calorimeter cells. For these measurements, the microcalorimeter was calibrated in situ using the reported standard molar enthalpy of sublimation of naphthalene 72.6±0.6 kJ mol^{-1} [19].

The observed enthalpies of sublimation were corrected to T=298.15 K, using the value of $\Delta_{298.15\ \mathrm{K}}^{457\ \mathrm{K}} H_{\mathrm{m}}^{0}(g)$ estimated by the Benson's Group Method [32], using values from Stull *et al.* [33].

Results and discussion

Results for all the combustion experiments are given in Table 1, where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 3116.3 g, and ΔU_{Σ} is the correction to the standard state. The remaining quantities are as previously described [26]. As samples were ignited at T=298.15 K,

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + \Delta m(\mathrm{H_2O})c_{\mathrm{p}}(\mathrm{H_2O},(l)) + \varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}} \tag{1}$$

The individual values of $\Delta_{\mathrm{c}}u^0$, registered in Table 1, are referred to the combustion reaction according to Eq. (2):

$$\mathrm{C_{14}H_9NO_2}(cr) + \frac{61}{4}\mathrm{O_2}(g) \rightarrow 14\mathrm{CO_2}(g) + \frac{1}{2}\mathrm{N_2}(g) + \frac{9}{2}\mathrm{H_2O}(l) \tag{2}$$

The derived standard (p^0=0.1 MPa) values for the molar energy and enthalpy of combustion, as well as the standard molar enthalpy of formation, at T=298.15 K, of crystalline *N*-phenylphthalimide are the following: $\Delta_{\mathrm{c}}U_{\mathrm{m}}^{0}(cr)$= –6587.5±2.8 kJ mol^{-1}, $\Delta_{\mathrm{c}}H_{\mathrm{m}}^{0}(cr)$= –6589.4±2.8 kJ mol^{-1} and $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}(cr)$= –206.0±3.4 kJ mol^{-1}. In accordance with normal thermochemical practice, the uncertainty assigned to the standard molar enthalpy of combustion is twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used. To derive $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}(cr)$ from $\Delta_{\mathrm{c}}H_{\mathrm{m}}^{0}(cr)$ the standard molar enthalpies of formation of $\mathrm{H_2O}(l)$ and $\mathrm{CO_2}(g)$, at T=298.15 K, respectively, –285.830±0.042 kJ mol^{-1} [34] and –393.51± 0.13 kJ mol^{-1} [34], were used.

Detailed results of the measurements of the enthalpy of sublimation are given in Table 2. From five independent determinations at T=457 K, the average value of the observed enthalpies of sublimation

Table 1 Standard (p^0=0.1 MPa) massic energy of combustion of *N*-phenylphthalimide, at T=298.15 K

	1	2	3	4	5	6	7	8
$m(\mathrm{CO_2})$/g	1.90755	1.92085	1.93414	2.28130	1.92693	1.90859	1.82238	1.85004
m(compound)/g	0.68875	0.69278	0.69845	0.82382	0.69581	0.68815	0.65711	0.66745
m(fuse)/g	0.00449	0.00575	0.00472	0.00494	0.00398	0.00571	0.00576	0.00515
ΔT_{ad}/K	1.28299	1.29238	1.30166	1.53433	1.29715	1.28437	1.22507	1.24558
ε_{f}/J K^{-1}	15.56	15.57	15.58	15.82	15.58	15.56	15.51	15.52
$\Delta m(\mathrm{H_2O})$/g	0.0	0.0	–0.1	0.0	0.0	0.0	0.0	–0.1
–ΔU(IBP)/J	20429.46	20579.01	20726.25	24432.26	20654.99	20451.44	19507.08	19833.18
–ΔU(carbon)/J	6.60	5.28	11.55	4.62	0	0	5.61	4.62
$\Delta U/(\mathrm{HNO_3})$/J	30.73	30.73	31.30	39.27	30.16	30.73	29.03	30.16
ΔU(ignition)/J	1.20	1.20	1.20	1.20	1.19	1.20	1.20	1.19
ΔU(fuse)/J	72.92	93.38	76.65	80.23	64.64	92.73	93.54	83.64
ΔU_{Σ}/J	15.32	15.47	15.60	18.74	15.50	15.34	14.56	14.82
–$\Delta_{\mathrm{c}}u^0$/J g^{-1}	29498.49	29511.10	29514.28	29495.08	29526.29	29517.75	29486.02	29529.07
$\langle\Delta_{\mathrm{c}}u^0\rangle$= –29509.8±5.4 J g^{-1}								

[a] ΔU(IBP) includes ΔU(ignition); $m(\mathrm{CO_2})$ is the mass of $\mathrm{CO_2}$ recovered in the combustion; m(compound) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_{f} is the energy equivalent of contents in the final state; $\Delta m(\mathrm{H_2O})$ is the deviation of mass of water added to the calorimeter from 3116.3; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(carbon) is the correction energy for carbon soot formation; $\Delta U(\mathrm{HNO_3})$ is the energy correction for the nitric acid formation; ΔU(ignition) is the electrical energy for ignition; ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU_{Σ} is the standard state correction; $\Delta_{\mathrm{c}}u^0$ is the standard massic energy of combustion

Table 2 Standard (p^0=0.1 MPa) molar enthalpy of sublimation of *N*-phenylphthalimide, at *T*=298.15 K

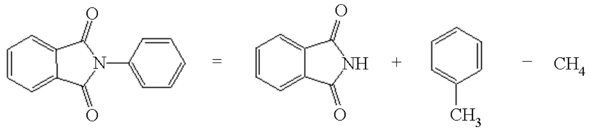
T/K	*m*/mg	$\Delta_{\mathrm{cr},\,298.15\,\mathrm{K}}^{\mathrm{g},T} H_{\mathrm{m}}^{0}$/kJ mol^{-1}	$\Delta_{298.15\,\mathrm{K}}^{T} H_{\mathrm{m}}^{0}(g)$/kJ mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{0}$(*T*=298.15 K)/kJ mol^{-1}
457.4	4.073	162.62	40.73	121.89
457.5	4.165	162.58	40.76	121.82
457.5	3.684	161.02	40.76	120.26
457.9	3.797	163.13	40.88	122.25
458.1	4.257	161.41	40.94	120.47

$\langle\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{0}(T=298.15\ \mathrm{K})\rangle=121.34\pm0.99\ \mathrm{kJ\ mol^{-1}}$

is $\Delta_{\mathrm{cr},\,298.15\,\mathrm{K}}^{\mathrm{g},\,457\,\mathrm{K}} H_{\mathrm{m}}$=162.15 kJ mol^{-1}. The standard molar enthalpy of sublimation, at *T*=298.15 K, is calculated by Eq. (3):

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{0}(T=298.15\ \mathrm{K})=\Delta_{\mathrm{cr},\,298.15\,\mathrm{K}}^{\mathrm{g},\,457\,\mathrm{K}} H_{\mathrm{m}}-\Delta_{298.15\,\mathrm{K}}^{457\,\mathrm{K}} H_{\mathrm{m}}^{0}(g) \tag{3}$$

using the enthalpic correction to the reference temperature *T*=298.15 K, $\Delta_{298.15\,\mathrm{K}}^{457\,\mathrm{K}} H_{\mathrm{m}}^{0}(g)$=40.81 kJ mol^{-1}, estimated by a group additivity method, i.e.,

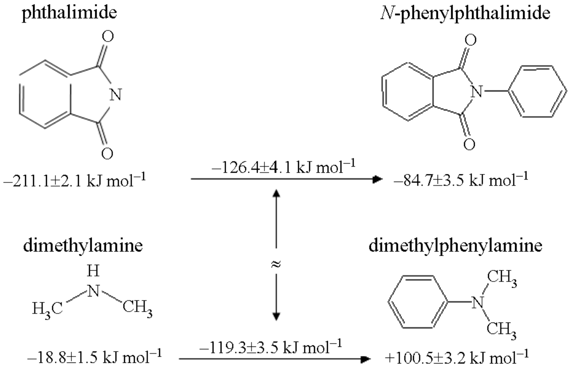


based on the values of Stull *et al.* [33], thus yielding the value of the standard molar enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{0}$(*T*=298.15 K) =121.34±0.99 kJ mol^{-1}.

From the values, at *T*=298.15 K, of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{0}(cr)$ and of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{0}$, the derived standard molar enthalpy of formation, in the gaseous phase, for *N*-phenylphthalimide is calculated as $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{0}(g)$= –84.7±3.5 kJ mol^{-1}.

Conclusions

From the literature data, the standard molar enthalpy of formation of phthalimide, in the gaseous state, at *T*=298.15 K, is –211.1±2.1 kJ mol^{-1} [1], from which one calculates that the enthalpic increment of the addition of a phenyl group to phthalimide, to yield *N*-phenylphthalimide, is –126.4±4.1 kJ mol^{-1}. The literature values for the standard molar enthalpies of formation, at *T*=298.15 K, of gaseous dimethylamine and dimethylphenylamine are, respectively, –18.8±1.5 kJ mol^{-1} [35] and +100.5±3.2 kJ mol^{-1} [35], from which the enthalpic increment for the dimethylamine→dimethylphenylamine transformation is calculated as –119.3±3.5 kJ mol^{-1}.



Scheme Enthalpic effects of the introduction of a phenyl group in the phthalimide and in the dimethylamine

As shown in the scheme, these two enthalpic increments for the addition of a phenyl group to the nitrogen atoms of phthalimide and of dimethylamine, to yield respectively, *N*-phenylphthalimide and dimethylphenylamine, do overlap within the assigned uncertainties, showing that the phenyl molecular increment does not introduce different specific enthalpic effects.

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This paper is dedicated to the memory of my good friend and colleague Professor Lisardo Núñez Regueira, who suddenly passed away recently, in recognition of our friendship of some decades and of the interest and work he has done on the developing of applied the research in the University of Santiago de Compostela and in Galícia.

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