



THERMOCHEMICAL STUDIES OF PHTHALIMIDE AND TWO *N*-ALKYLSUBSTITUTED PHTHALIMIDES (*ALKYL*=ETHYL AND *n*-PROPYL)

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The standard ($p^0=0.1$ MPa) molar enthalpies of formation, $\Delta_f H_m^0$, for crystalline phthalimides: phthalimide, *N*-ethylphthalimide and *N*-propylphthalimide were derived from the standard molar enthalpies of combustion, in oxygen, at the temperature 298.15 K, measured by static bomb-combustion calorimetry, as, respectively, $-(318.0 \pm 1.7)$, $-(350.1 \pm 2.7)$ and $-(377.3 \pm 2.2)$ kJ mol⁻¹. The standard molar enthalpies of sublimation, $\Delta_{cr}^s H_m^0$, at $T=298.15$ K were derived by the Clausius-Clapeyron equation, from the temperature dependence of the vapour pressures for phthalimide, as (106.9 ± 1.2) kJ mol⁻¹ and from high temperature Calvet microcalorimetry for phthalimide, *N*-ethylphthalimide and *N*-propylphthalimide as, respectively, (106.3 ± 1.3) , (91.0 ± 1.2) and (98.2 ± 1.4) kJ mol⁻¹.

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

Keywords: combustion calorimetry, Knudsen effusion, *N*-ethylphthalimide, *N*-propylphthalimide, phthalimide, standard molar enthalpy of formation, standard molar enthalpy of sublimation, vapour pressures

Introduction

Our research group has been involved in a systematic experimental and theoretical study on the energetics of nitrogen heterocycles. Nitrogen heterocycle compounds are important part of the chemical structures of many natural and synthetic products with a large number and variety of applications and a wide range of properties, from medical to toxic effects. Among the bicyclic non-aromatic nitrogen heterocycles, phthalimides are an interesting class of compounds with a large range of applications. Phthalimides have served as starting materials and intermediates for the synthesis of many types of alkaloids and pharmacophores [1]. The phthalimide group has also provided the classical means for direct introduction of the masked amino functions as well as for *N*-protection of amino acids, amino sugars and simple amino alcohols [2, 3]. Polymers containing phthalimide groups are found to possess excellent heat resistance and transparency [4], copolymers containing the phthalimide derivatives have been used as optical brightening agents [5] and *N*-substituted phthalimide copolymers may be used as activated drug binding materials [6]. *N*-substituted phthalimides are also used in the synthesis of pesticides, mainly insecticides, herbicides and fungicides [7]. Recently, phthalimide and some

of its derivatives have proved to have important biological effects, similar or even higher, than known pharmacological molecules, and so are being subject of intense biomedical research [8–10].

Despite their importance, very little information is known on the energetics of phthalimides. The literature reports two different values to the standard molar enthalpy of formation of the crystalline phthalimide: -305.4 kJ mol⁻¹ [11] and $-(318.2 \pm 2.1)$ kJ mol⁻¹ [12], determined by combustion calorimetry. In view of such considerable difference between the two literature values, we extended our thermochemical study to the redetermination of this enthalpy of formation, besides measuring the enthalpy of sublimation of the phthalimide, at $T=298.15$ K, a property for which the literature reports a value of 82.8 kJ mol⁻¹ [13] measured by the Rodebush gauge in the temperature range 378–418 K. The literature reports also, the standard molar enthalpy of formation of *N*-methylphthalimide in the crystalline state as $-(325.0 \pm 2.1)$ kJ mol⁻¹ [14, 15] and its standard molar enthalpy of sublimation as (91.1 ± 0.5) kJ mol⁻¹ [14, 15] determined, respectively, by static bomb combustion calorimetry and measurements of vapour pressures as function of temperature, by Knudsen effusion.

The present work reports the experimental results of thermochemical studies of phthalimide

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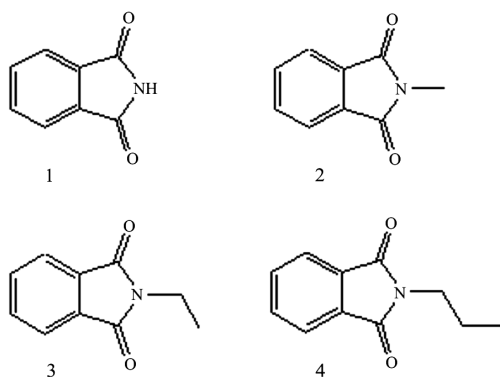


Fig. 1 Structural formula for 1 – phthalimide, 2 – *N*-methylphthalimide, 3 – *N*-ethylphthalimide and 4 – *N*-propylphthalimide

[CAS 85-41-6] and two *N*-alkylphthalimides: *N*-ethylphthalimide [CAS 5022-29-7] and *N*-propylphthalimide [CAS 5323-50-2], whose structural formulae are represented in Fig. 1.

The standard ($p^0=0.1$ MPa) molar enthalpies of combustion, $\Delta_c H_m^0$ in oxygen, at $T=298.15$ K, were determined by static-bomb calorimetry, and the standard molar enthalpies of sublimation were derived, at the same temperature, by the Knudsen effusion method or by Calvet microcalorimetry. The derived values of the standard molar enthalpies of formation for the compounds in the gaseous state, are analysed in terms of enthalpic increments due to the introduction of methylene groups in the alkyl chain of *N*-alkylphthalimides.

Experimental

Compounds and purity control

Phthalimide of 99.80% purity, obtained commercially from Aldrich Chemical Co., *N*-ethylphthalimide and *N*-propylphthalimide purchased from Lancaster Synthesis, both with a purity of 98%, were purified by vacuum sublimation until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratios, together with the standard deviations of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample were: phthalimide, (1.0001 \pm 0.0001); *N*-ethylphthalimide (0.9994 \pm 0.0002) and *N*-propylphthalimide (0.9998 \pm 0.0002), where the uncertainties are the standard deviation of the mean. The purity of each compound was also checked by differential scanning calorimetry.

Combustion calorimetry

The combustion experiments were performed with an isoperibolic static-bomb calorimeter; apparatus and

technique have been described [16, 17]. Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard CRM-190p) was used for calibration of the bomb. Its massic energy of combustion, under bomb conditions, is $-(26435.1\pm 3.5)$ J g⁻¹. 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. The energy equivalent of the calorimeter was determined, as $\epsilon_{\text{calor}}=(15908.7\pm 1.3)$ J K⁻¹, from the average of 18 independent experiments, where the uncertainty quoted is the standard deviation of the mean. For all experiments, ignition was made at $T=(298.150\pm 0.001)$ K. Combustion experiments were made in oxygen at the pressure 3.04 MPa, with a volume 1 cm³ of water added to the bomb. The crystalline compounds were burnt in pellet form.

Calorimeter temperatures were measured to $\pm(1\cdot 10^{-4})$ K at time intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz crystal thermometer, interfaced to an Olivetti M 250E microcomputer: 100 readings were taken for the main period and for both the fore period and the after period. 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, empirical formula CH_{1.686}O_{0.843}, $\Delta_c u^0 = -16250$ J g⁻¹ [18], a value which was confirmed in our laboratory. The corrections for nitric acid formation were based on -59.7 kJ mol⁻¹ for the molar energy of formation of 0.1 mol dm³ HNO₃(aq) from 1/2N₂(g), 3/2O₂(g) and H₂O(l) [19]. Corrections for carbon residue soot formation were based on $\Delta_c u^0 = -33$ kJ g⁻¹, [18]; an estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2$ J g⁻¹ MPa⁻¹, at $T=298.15$ K, a typical value for most organic compounds [20], was assumed. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton-thread fuse and that lost due to carbon formation. All the necessary weighing was made in a Mettler Toledo AT 201 balance, sensitivity $\pm(1\cdot 10^{-4})$ g, and corrections from apparent mass to true mass were made. For each compound, $\Delta_c u^0$ was calculated by a similar procedure to that developed by Hubbard *et al.* [18].

Vapour pressures measurements

The vapour pressures of phthalimide were measured at several temperatures using a Knudsen effusion apparatus enabling the simultaneous operation of nine effusion cells at three different temperatures. The apparatus has been tested by measuring vapour pressures between 0.1 and 1 Pa, over temperature ranges of ca. 20 K, of benzoic acid, phenanthrene, anthracene, benzanthrone and

1,3,5-triphenylbenzene [21]. Both the measured vapour pressures and the derived enthalpies of sublimation were in excellent agreement with literature results and recommended values for those compounds. The nine effusion cells are contained in cylindrical holes inside three aluminium blocks. During an effusion experiment, each aluminium block is kept at a constant temperature, different from the other two blocks, and contains three effusion cells with effusion orifices of different areas – one ‘small’ ($A_0 \approx 0.5 \text{ mm}^2$; series A), one ‘medium’ ($A_0 \approx 0.8 \text{ mm}^2$; series B) and one ‘large’ ($A_0 \approx 1.1 \text{ mm}^2$; series C). The exact areas and Clausing factors of each used effusion orifice in platinum foil of 0.0125 mm thickness are given in reference [21].

For the temperature T , the vapour pressure p of the crystalline sample contained in each effusion cell is calculated by Eq. (1), where m is the sublimed mass during the effusion time period t , M is the molar mass of the effusing vapour, R is the gas constant, A_0 is the area of the effusion orifice and w_0 is the respective Clausing factor.

$$p = (m/A_0 w_0 t)(2\pi RT/M)^{1/2} \quad (1)$$

High temperature microcalorimetry

The enthalpies of sublimation of the compounds were measured using the ‘vacuum sublimation’ drop microcalorimetric method [22, 23]. Each sample, contained in a small thin glass capillary tube sealed at one end, was dropped at room temperature into the hot re-

action vessel in the Calvet High-Temperature Microcalorimeter (Setaram, Lyon, France) held at a predefined temperature and then removed from the hot zone by vacuum sublimation. Simultaneously a similar empty capillary tube was dropped in the reference cell. The observed enthalpies of sublimation were corrected to $T=298.15 \text{ K}$ using $\Delta_{298.15 \text{ K}}^T H_m^0(g)$ estimated by a group method based on the values of Stull *et al.* [24]. The microcalorimeter was calibrated in situ for these measurements using the reported enthalpies of sublimation of naphthalene [25].

The relative atomic masses were those recommended by the IUPAC in 2001 [26].

Results and discussion

Detailed results for a typical combustion experiment of each compound are given in Table 1, where $\Delta m(\text{H}_2\text{O})$ 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 terms have been previously described [18]. The results of the massic energies of combustion, $\Delta_c u^0$, for all the combustion experiments done, together with the mean values and their standard deviations, are given, for each compound, in Table 2.

Table 3 lists the derived standard molar energies ($\Delta_c U_m^0$) and enthalpies ($\Delta_c H_m^0$) of combustion, referred to the combustion reaction of phthalimides accordingly to Eq. (2), as well as the standard molar

Table 1 Results of a typical combustion experiment, for each compound, at $T=298.15 \text{ K}$

	Phthalimide	<i>N</i> -Ethylphthalimide	<i>N</i> -Propylphthalimide
$m(\text{CO}_2, \text{total})/\text{g}$	2.02777	1.81104	1.80938
$m'(\text{cpd})/\text{g}$	0.84400	0.71797	0.70393
$m''(\text{fuse})/\text{g}$	0.00532	0.00457	0.00516
$\Delta T_{\text{ad}}/\text{K}$	1.28622	1.26088	1.29789
$\varepsilon_f/\text{J K}^{-1}$	15.65	15.87	16.4
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	-0.1	-0.1
$-\Delta U(\text{IBP})^{\text{a}}/\text{J}$	20482.22	20078.44	20668.02
$\Delta U(\text{fuse})/\text{J}$	86.40	74.22	83.80
$\Delta U(\text{HNO}_3)/\text{J}$	37.63	31.36	31.30
$\Delta U(\text{ign})/\text{J}$	1.20	1.20	1.19
$-\Delta U(\text{carbon})/\text{J}$	4.29	0.0	0.0
$\Delta U_{\Sigma}/\text{J}$	18.35	14.48	13.82
$-\Delta_c u^0/\text{J g}^{-1}$	24102.88	27796.84	29175.91

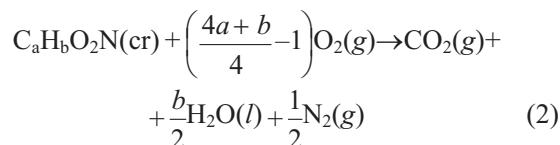
^a $\Delta U(\text{IBP})$ already includes the $\Delta U(\text{ign})$; $m(\text{CO}_2)$ is the mass of CO_2 recovered in the combustion; $m(\text{cpd.})$ is the mass of compound burnt in each experiment; $m(\text{fuse})$ is the mass of fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of contents in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 3119.6 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electrical energy for ignition; $\Delta U(\text{carbon})$ is the energetic correction for the formation of carbon residue soot; ΔU_{Σ} is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion

Table 2 Individual values of the massic energy of combustion, $-\Delta_c u^0$, of the compounds at $T=298.15$ K

$-\Delta_c u^0/\text{J g}^{-1}$		
Phthalimide	<i>N</i> -ethylphthalimide	<i>N</i> -propylphthalimide
24094.60	27812.10	29182.15
24085.86	27785.34	29175.91
24100.72	27785.09	29170.53
24102.88	27814.18	29189.90
24083.27	27796.84	29162.76
24104.30	27776.83	29172.29
		29165.95
		29179.41
$-\langle\Delta_c u^0\rangle^a/\text{J g}^{-1}$		
24095.3±3.7	27795.1±6.3	29174.9±3.1

^aMean value and standard deviation of the mean

enthalpies of formation for the compounds, in the crystalline phase, at $T=298.15$ K. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration [27] and in values of auxiliary quantities.

**Table 3** Derived standard ($p^0=0.1$ MPa) molar energies of combustion, $\Delta_c U_m^0$, standard molar enthalpies of combustion, $\Delta_c H_m^0$, and standard molar enthalpies of formation, $\Delta_f H_m^0$, for the compounds at $T=298.15$ K

	$-\Delta_c U_m^0(\text{cr})/\text{kJ mol}^{-1}$	$-\Delta_c H_m^0(\text{cr})/\text{kJ mol}^{-1}$	$-\Delta_f H_m^0(\text{cr})/\text{kJ mol}^{-1}$
Phthalimide	3545.2±1.3	3544.6±1.3	318.0±1.7
<i>N</i> -ethylphthalimide	4869.3±2.4	4871.2±2.4	350.1±2.7
<i>N</i> -propylphthalimide	5520.3±1.7	5523.4±1.7	377.3±2.2

Table 4 Knudsen Effusion experimental results. The sublimed mass and the pressure results related to the small (A_1, A_2, A_3), medium (B_4, B_5, B_6) and large (C_7, C_8, C_9) orifices are denoted, respectively, by the subscripts *s*, *m* and *l*

Temperature/K	Time/s	Orifices	<i>m</i> /mg			<i>p</i> /Pa		
			<i>m_s</i>	<i>m_m</i>	<i>m_l</i>	<i>p_s</i>	<i>p_m</i>	<i>p_l</i>
347.12	18383	A ₁ , B ₄ , C ₇	4.35	6.52	9.51	0.167	0.162	0.164
349.24	18383	A ₂ , B ₅ , C ₈	5.45	8.44	11.74	0.212	0.208	0.201
351.28	18383	A ₃ , B ₆ , C ₉	6.54	10.15	14.60	0.256	0.255	0.246
353.28	11706	A ₃ , B ₆ , C ₉	5.17	7.99	11.45	0.319	0.316	0.304
355.25	11706	A ₂ , B ₅ , C ₈	6.27	9.59	13.61	0.385	0.375	0.370
357.13	11706	A ₁ , B ₄ , C ₇	7.40	11.43	16.17	0.453	0.454	0.444
359.10	10294	A ₁ , B ₄ , C ₇	7.91	12.08	17.31	0.553	0.547	0.542
361.22	10294	A ₂ , B ₅ , C ₈	9.87	15.11	20.95	0.696	0.677	0.653
363.27	10294	A ₃ , B ₆ , C ₉	11.72	18.19	25.89	0.833	0.829	0.792
365.10	8768	A ₁ , B ₄ , C ₇	11.81	18.13	25.56	0.977	0.972	0.948

To derive $\Delta_f H_m^0(\text{cr})$ from $\Delta_c H_m^0$, the following standard molar enthalpies of formation, at $T=298.15$ K, were used for $\text{H}_2\text{O}(\text{l})$, $-(285.830\pm 0.042)$ kJ mol⁻¹ [28], and for $\text{CO}_2(\text{g})$, $-(393.51\pm 0.13)$ kJ mol⁻¹ [28].

Table 4 presents the experimental results obtained through the effusion experiments. The subscripts A, B, C of the variables *m* and *p* stand, respectively, for the results obtained through the small (A_1, A_2, A_3), the medium (B_4, B_5, B_6) and the large (C_7, C_8, C_9) effusion orifices.

Table 5 presents, for each series of effusion orifices (A, B, C) the parameters of the Clausius–Clapeyron equation, $\ln(p/\text{Pa})=a-b/T$, where *a* is a constant and $b=\Delta_{\text{cr}}^{\text{g}} H_m^0(\langle T \rangle)/R$, and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T=\langle T \rangle$. Figure 2 shows the plot of $\ln p$ vs. $1/T$, for the experimental data obtained with the three sets of effusion cells. As can be noticed from the values of the pressures at the mean experimental temperatures also presented in this table, there is a slight decrease of the measured vapour pressures with the increasing area of the effusion orifices. The equilibrium pressure at each experimental temperature was determined by plotting p_i vs. $(p_i w_0 A_0)$, where p_i represents the vapour pressures derived at each effusion temperature from the Clausius–Clapeyron equations. According to an equation developed by Whitman [29] and Motzfeldt [30] the intercepts of the derived straight lines at zero area, may be considered the equilibrium pressures. The values of the parameters derived from

Table 5 Results derived from the effusion experiments for phthalimide, where a and b are from Clausius–Clapeyron equation $\ln(p/\text{Pa})=a-b(K/T)$, and $b=\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(<T>)/R$; $R=8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$

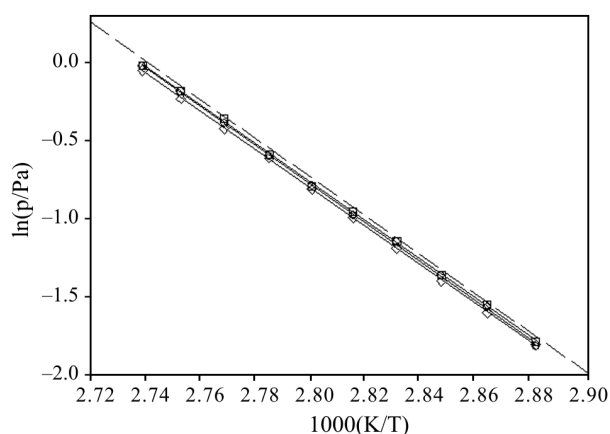
Effusion orifices	a	b	$\langle T \rangle/\text{K}$	$p(\langle T \rangle)/\text{Pa}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(<T>)/\text{kJ mol}^{-1}$
A	34.07±0.24	12445±87		0.416	103.5±0.7
B	34.31±0.13	12536±82		0.410	104.2±0.7
C	33.91±0.14	12401±49		0.401	103.1±0.4
Mean	34.10±0.10	12461±43	356.11	0.410	103.6±0.4
Zero area	34.30±0.10	12514±43	356.11	0.431	104.0±0.4

Table 6 Microcalorimetric standard ($p^0=0.1 \text{ MPa}$) molar enthalpies of sublimation at $T=298.15 \text{ K}$

	Number of experiments	T/K	$\Delta_{\text{cr},298 \text{ K}}^{\text{g}}H_{\text{m}}^0/\text{kJ mol}^{-1}$	$\Delta_{298.15 \text{ K}}^{\text{g}}H_{\text{m}}^0(\text{g})/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(T=298.15 \text{ K})/\text{kJ mol}^{-1}$
Phthalimide	5	458.0	132.13±1.33	25.80	106.33±1.33
<i>N</i> -ethylphthalimide	6	358.2	102.44±1.16	11.49	90.95±1.16
<i>N</i> -propylphthalimide	7	348.0	109.06±1.37	10.86	98.20±1.37

Table 7 Derived standard ($p^0=0.1 \text{ MPa}$) molar enthalpies of formation, $\Delta_{\text{f}}H_{\text{m}}^0$, and of sublimation, $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0$, at $T=298.15 \text{ K}$

	$-\Delta_{\text{f}}H_{\text{m}}^0(\text{cr})/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0/\text{kJ mol}^{-1}$	$-\Delta_{\text{f}}H_{\text{m}}^0(\text{g})/\text{kJ mol}^{-1}$
Phthalimide	318.0±1.7	106.9±1.2	211.1±2.1
<i>N</i> -ethylphthalimide	350.1±2.7	91.0±1.2	259.1±3.0
<i>N</i> -propylphthalimide	377.3±2.2	98.2±1.4	279.1±2.6


Fig. 2 Plots of $\ln p$ vs. $1/T$ for the phthalimide. \square – small effusion orifices; \circ – medium effusion orifices; \diamond – large effusion orifices; the dashed line represents the linear regression on the equilibrium vapor pressures (zero area)

the equilibrium pressures using the Clausius–Clapeyron equation are also presented in Table 5 after ‘zero area’ and were selected to calculate the enthalpy of sublimation which equals, within experimental uncertainty, the mean of the enthalpies of sublimation derived from the results obtained with each series of the effusion orifices. Using the estimated [31] value $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^0 = -(50 \pm 20) \text{ J mol}^{-1} \text{ K}^{-1}$, in the Eq. (3), the value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(T=298.15 \text{ K}) = (106.9 \pm 1.2) \text{ kJ mol}^{-1}$ was derived.

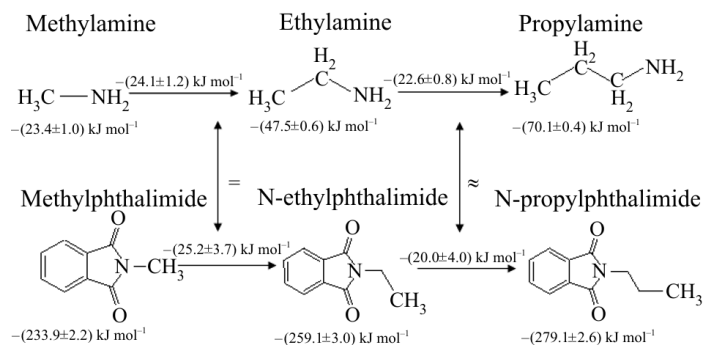
$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(T=298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(\langle T \rangle) + \Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^0(298.15 \text{ K} - \langle T \rangle) \quad (3)$$

Results for the enthalpies of sublimation, determined by the vacuum sublimation technique with the Calvet high temperature microcalorimeter, are given in Table 6 with uncertainties of twice the standard deviation of the mean. As it is seen, the values obtained for $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^0(T=298.15 \text{ K})$ of phthalimide, by the Knudsen effusion technique and the Calvet microcalorimetry, are equal, which gives additional confidence to the values of the enthalpies of sublimation of the other compounds determined by Calvet microcalorimetry. The value derived from the Knudsen effusion technique is the one which will be used in further calculations in this paper.

The derived standard molar enthalpies of formation in the condensed phase, standard molar enthalpies of sublimation, and standard molar enthalpies of formation in the gaseous state are summarised in Table 7.

Conclusions

The standard molar enthalpies of formation, $\Delta_{\text{f}}H_{\text{m}}^0$, of the *N*-alkylsubstituted phthalimides, in the gaseous phase, at $T=298.15 \text{ K}$, yield the enthalpic increments for the introduction of a methylene group in the alkyl chain of the compounds as follows: $-(22.8 \pm 3.0) \text{ kJ mol}^{-1}$ for the transformation of phthalimide \rightarrow *N*-methylphthalimide, $-(25.2 \pm 3.7) \text{ kJ mol}^{-1}$ for the transformation of *N*-methylphthalimide \rightarrow *N*-ethylphthalimide, and $-(20.0 \pm 4.0) \text{ kJ mol}^{-1}$ for the transformation of *N*-ethyl-



Scheme 1

phthalimide \rightarrow N-propylphthalimide. From the literature values [32] for $\Delta_f H_m^0$ of the *n*-alkanes it is shown that the average enthalpic increment of the addition of a methylene group in the *n*-alkanes is $-22.76 \text{ kJ mol}^{-1}$, which is the same as the increment for the transformation *N*-ethylphthalimide \rightarrow *N*-propylphthalimide, although somewhat smaller than the identical increment for the *N*-methylphthalimide \rightarrow *N*-ethylphthalimide transformation.

From the literature [32], the standard molar enthalpies of formation, in the gaseous state, of methylamine, ethylamine and *n*-propylamine are, respectively, $-(23.4 \pm 1.0)$, $-(47.5 \pm 0.6)$ and $-(70.1 \pm 0.4) \text{ kJ mol}^{-1}$, from where it is seen that the enthalpic increment for the entrance of a methylene group in methylamine is $-(24.1 \pm 1.2) \text{ kJ mol}^{-1}$, in good agreement with identical enthalpic increment in the transformation *N*-methylphthalimide \rightarrow *N*-ethylphthalimide.

As shown in Scheme 1, these enthalpic increments for the addition of methylene groups in the primary amines are in agreement with the enthalpic increments for identical additions in *N*-alkylsubstituted phthalimides and *n*-alkanes.

In conclusion, the addition of methylene groups in the chains of *n*-alkanes, primary amines and *N*-alkylamines has a monotonic enthalpic effect, showing that such molecular increments do not induce different specific enthalpic effects.

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References

- 1 F. A. Luzzio and De A. P. Zacherl, *Tetrahedron Lett.*, 40 (1999) 2087.
- 2 T. W. Green and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd Ed., John Wiley and Sons, New York 1991, p. 309.
- 3 J. S. Debenham, R. Madsen, C. Roberts and B. Freiser-Reid, *J. Am. Chem. Soc.*, 117 (1995) 3302.
- 4 R. Jayakumar, R. Balaji and S. Nanjundan, *Eur. Polym. J.*, 36 (2000) 1659.
- 5 T. N. Constantinova and I. K. Garbechev, *Polym. Int.*, 43 (1998) 43.
- 6 M. Ismail, V. Veena and K. R. Animesh, *J. Appl. Polym. Sci.*, 68 (1998) 217.
- 7 <http://www.alanwood.net/pesticides>
- 8 L. M. Lima, F. C. F. Brito, S. D. Souza, A. L. P. Miranda, C. R. Rodrigues, A. M. Fraga and E. J. Barreiro, *Bioorg. Med. Chem. Lett.*, 12 (2002) 1533.
- 9 H. Miyachi, A. Azuma, A. Ogasawara, E. Uchimura, N. Watanabe, Y. Kobayashi, F. Kato and Y. Hashimoto, *J. Med. Chem.*, 40 (1997) 2858.
- 10 V. L. M. Sena, M. Srivastava, R. O. Silva and V. L. M. Luis, *Il Farmaco*, 58 (2003) 1283.
- 11 M. S. Kharasch, *J. Res. Natl. Bur. Std.*, 2 (1929) 359.
- 12 A. Charlton and J. I. Macnab, *Thermochim. Acta*, 344 (2000) 15.
- 13 E. J. Barber and G. H. Cady, *J. Phys. Chem.*, 60 (1956) 504.
- 14 M. V. Roux, P. Jiménez, M. A. Martin-Luengo, J. Z. Dávalos, Z. San, R. S. Hosmane and J. F. Liebman, *J. Org. Chem.*, 62 (1997) 2732.
- 15 M. V. Roux, P. Jiménez, J. Z. Dávalos, M. A. Martin-Luengo, V. M. Rotello, A. O. Cuello and J. F. Liebman, *Struct. Chem.*, 11 (2000) 1.
- 16 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *Rev. Port. Quim.*, 26 (1984) 163.
- 17 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *J. Chem. Thermodyn.*, 16 (1984) 1149.
- 18 W. N. Hubbard, D. W. Scott and G. Waddington, in: F. D. Rossini (Ed). *Experimental Thermochemistry*, Vol. 1, Interscience, New York 1956, Chapter 5.
- 19 The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, 11 (1982) (Supp. 2).
- 20 E. N. Washburn, *J. Res. Natl. Bur. Stand. (U.S.)*, 10 (1933) 525.

- 21 M. A. V. Ribeiro da Silva, M. J. S. Monte and L. M. N. B. F. Santos, *J. Chem. Thermodyn.*, 2005, in press, DOI:10.1016/j.jct.2005.08.013.
- 22 A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, *J. Organomet. Chem.*, 97 (1975) 221.
- 23 L. M. N. B. F. Santos, B. Schröder, O. O. P. Fernandes and M. A. V. Ribeiro da Silva, *Thermochim. Acta*, 415 (2004) 15.
- 24 D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York 1969.
- 25 C. G. de Kruif, T. Kuipers, J. C. Van Miltenburg, R. C. F. Schaake and G. Stevens, *J. Chem. Thermodyn.*, 13 (1981) 1081.
- 26 R. D. Loss, *Pure Appl. Chem.*, 75 (2003) 1107.
- 27 F. D. Rossini, in: F. D. Rossini (Ed.) *Experimental Thermochemistry*, Vol. 1, Interscience, New York 1956, Chapter 14.
- 28 J. D. Cox, D. D. Wagman and V. A. Medvedev, *CODATA Key Values for Thermodynamics*. Hemisphere, New York 1989.
- 29 C. J. Whitman, *J. Chem. Phys.*, 20 (1952) 161.
- 30 K. Motzfeldt, *J. Phys. Chem.*, 59 (1955) 139.
- 31 P. M. Burkinshaw and C. T. Mortimer, *J. Chem. Soc., Dalton Trans.*, (1984) 75.
- 32 J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds*, Vol. 1, Thermodynamics Research Center, College Station: TX, 1994.

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