The effect of ketone groups on the energetic properties of phthalan derivatives

Vera L.S. Freitas, Cláudia P.F. Santos [1], Maria D.M.C. Ribeiro da Silva *, Manuel A.V. Ribeiro da Silva

Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

ABSTRACT

In the present work the energetic properties of phthalide and phthalic anhydride are assessed experimental and computationally allowing to calculate the standard molar enthalpy of formation, in the gaseous phase, of each compound. These results enabled to analyze and interpret the enthalpic and structural molecular effects of one and two ketone groups in the main structure of phthalan.

The high-temperature Calvet microcalorimetry and the static bomb combustion calorimetry were used to measure, respectively, the enthalpy of sublimation and the massic energy of combustion of the two compounds. These data were combined to derive the standard molar enthalpy of formation, in the gaseous phase, of phthalide and phthalic anhydride.

The gas-phase enthalpies of formation of phthalide and phthalic anhydride compounds were estimated using the composite G3(MP2)//B3LYP approach together with adequate gas-phase working reactions. The computational study was also extended to phthalan and the reliability of the value obtained for the correspondent gas-phase enthalpy of formation, when compared with the experimental value reported in the literature, contributes to validate the computational methodology used. The good agreement verified between computational and experimental results for the other two phthalan derivatives studied gave us confidence to estimate the gas-phase enthalpy of formation of the 2,5-dihydrofuran that was not studied experimentally.

Complementary, natural bond orbital (NBO) calculations were also performed, allowing an advance on the analysis of the structural and reactivity characteristics of this type of compounds.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The extensive experimental and theoretical energetic study developed in our research group, involving a significant number of heterocyclic compounds, has been providing data used in the establishment of correlations between the molecular structure of the compounds and the respective energy contents, allowing their use in the prediction of data for related structures. This article follows previous researches on related heterocyclic compounds [1–3] and presents an experimental and computational study of phthalide (or isobenzofuran-1(3H)-one) and phthalic anhydride (or isobenzofuran-1,3-dione), complemented by a computational study of phthalan (or 1,3-dihydroisobenzofuran) and 2,5-dihydrofuran. The main structure of these phthalan derivatives is

bicyclic, presenting a benzenic ring fused to the tetrahydrofuran; the phthalide and phthalic anhydride (known as gama-lactones) have, respectively, one and two ketone functional groups attached to the heteroatomic ring, as it is evidenced in figure 1.

The phthalan molecule constitutes the main structure for a variety of more complex chemical compounds used as dyes [4], fungicides [5], polyester resins [6], natural oils [7], antidepressant drugs [8], among others. In which concerns the industrial applications phthalic anhydride is used in large-scale in the production of plasticizers. The knowledge of accurate thermodynamic data is relevant for the assessment of the feasibility of chemical processes and for the proposal of new and particularly more efficient synthetic routes.

Table 1 contains a compilation of thermochemical and thermophysical data available in the literature for the phthalan derivatives studied [9–16], namely values of the enthalpy of sublimation and enthalpy of formation, in the crystalline and gaseous phases, at the reference temperature $T = 298.15$ K. In this work, new experimental determinations were performed for phthalide and phthalic anhydride accompanied by computational studies using the G3

* Corresponding author. Tel.: + 351 220 402 538; fax: +351 220 402 659.
  E-mail address: mdsilva@fc.up.pt (M.D.M.C. Ribeiro da Silva).
[1] Present address: Universidade Federal de Campina Grande, Centro de Educação e Saúde, Unidade Acadêmica de Biologia e Química, Sítio Olho Dágua da Bica, s/n Campus Universitário, Cuité, PB CEP 58175-000, Brazil.
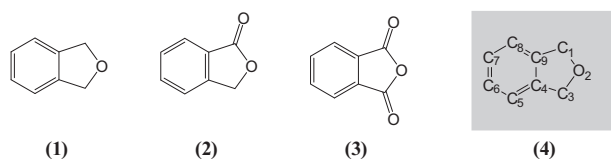
FIGURE 1. Molecular formula of phthalan (**1**), phthalide (**2**), and phthalic anhydride (**3**). The numbering of the atoms is evidenced in (**4**) for the basic structure.

(MP2)//B3LYP approach [17]. Extensive thermodynamic experimental data for phthalan were reported by Steele *et al.* [9] (table 1), leading us to perform calculations to this compound with the main goal of validating the computational methodology. The theoretical data of the gas-phase enthalpy of formation of 2,5-dihydrofuran reported by Dorofeeva [18] and Lay *et al.* [19] obtained by computational studies, respectively, $-(70.0$ and $87.4) \, \text{kJ} \cdot \text{mol}^{-1}$, led to incoherent results. This reason prompted us to estimate, also, the gas-phase enthalpy of formation of 2,5-dihydrofuran, by the same computational procedure.

The experimental studies were performed by static bomb calorimetry and drop-microcalorimetry, enabling to derive, respectively, the standard ($p° = 0.1 \, \text{MPa}$) molar enthalpy of formation, in the crystalline phase, $\Delta_f H_m^o(\text{cr})$, and the standard molar enthalpy of sublimation, $\Delta_{cr}^g H_m^o$, at $T = 298.15$ K. The combination of these two experimental parameters provided the value of the gas-phase standard molar enthalpy of formation, $\Delta_f H_m^o(\text{g})$, at the reference temperature, for phthalide and phthalic anhydride.

The computational studies were developed using the composite G3(MP2)//B3LYP method [17]. This approach provided the global minimum optimized structures and corresponding energies of the compounds studied, and also of other auxiliary species that were employed in the hypothetical gas-phase substitution group reactions used in the calculation of the $\Delta_f H_m^o(\text{g})$ values, at $T = 298.15$ K, for the compounds under study. The computational and experimental data are compared and discussed in terms of enthalpic effects. The computational work was also extended to the attainment of gas-phase molar heat capacities at different temperatures, dipole moment, electrostatic potential energy maps mapped onto electron density isosurface, and frontier orbitals.

2. Experimental methods

2.1. Materials, purification procedure and pureness control

The compounds used in the calibration of the calorimetric systems were: naphthalene, CAS Registry No. 91-20-3 (scintillation grade, 99+%), got commercially from Aldrich Chemical Co., and benzoic acid, CAS Registry No. 65-85-0, from BDH Thermochemical Standard, batch 693976/01 [21].

The crystalline samples of phthalide, CAS Registry No. 87-41-2, and phthalic anhydride, CAS Registry No. 85-44-9, purchased from Aldrich Chemical Co. with initial molar fraction purities higher than 0.99, were purified by vacuum sublimation; their purification and provenience details are summarized in table 2.

The purities of the samples were controlled by the ratio of carbon dioxide recovered (gravimetric analysis) in the combustion experiments (Section 2.2), until the ratio values were satisfactory and the energetic values consistent.

2.2. Combustion calorimetry

The standard ($p° = 0.1 \, \text{MPa}$) massic energies of combustion, $\Delta_c u^o$, of the compounds were measured by static-bomb combustion calorimetry. The combustion experiments were performed using an isoperibol calorimeter system equipped with a static bomb (Parr instrument, model 1105) having an internal volume of $0.340 \, \text{dm}^3$; apparatus and procedure have been described [22,23].

Crystalline samples of phthalide and phthalic anhydride were prepared in the pellet form and ignited at temperature of 298.15 K, in oxygen, at a pressure $p = 3.04$ MPa (purged twice to remove air), with a volume of $1.00 \, \text{cm}^3$ of deionised water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharge through the platinum ignition wire. After the calorimetric measurements, the combustion products were checked for traces of incomplete combustion and the nitric acid formed (from traces in the oxygen used in the filling of the bomb) was quantified by acid-base volumetric titrations and the total mass of carbon dioxide, formed in the experiments and collected in absorption

TABLE 1
Thermochemical and thermophysical values at $T = 298.15$ K reported in the literature for phthalan, phthalide, and phthalic anhydride.

Compound	$\Delta_f H_m^o(\text{cr,l})/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{cr,l}^g H_m^o/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_m^o(\text{g})/\text{kJ} \cdot \text{mol}^{-1}$
Phthalan (l)	-83.8 ± 0.9 [9]	53.7 ± 0.4 [9]	-30.1 ± 1.0 [9]
Phthalide (cr)	-366.0^a [10]		
Phthalic anhydride (cr)	-460.37^a [11]	88.7 ± 2.3 [12,16]	
		$90.4^{a,b}$	
		87.9 ± 1.2^c	
		87.6 ± 1.0^d	

[a] The standard deviation of the mean was not available.
[b] Original value $\Delta_{cr}^g H_m^o = 87.9 \, \text{kJ} \cdot \text{mol}^{-1}$ [13] (temperature range: 313 to 383 K) corrected for $T = 298.15$ K using the $\Delta_{cr}^g C_{p,m}^o$, calculated as $-(50 \pm 20) \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ according to estimations made by Burkinshaw and Mortimer [20].
[c] Original value $\Delta_{cr}^g H_m^o = 84.4 \pm 1.2 \, \text{kJ} \cdot \text{mol}^{-1}$ [14] (temperature range: 333 to 403 K) corrected for $T = 298.15$ K using the $\Delta_{cr}^g C_{p,m}^o$, calculated as $-(50 \pm 20) \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ according to estimations made by Burkinshaw and Mortimer [20].
[d] Original value $\Delta_{cr}^g H_m^o = 81 \pm 1 \, \text{kJ} \cdot \text{mol}^{-1}$ [15] (temperature range: 390 to 470 K) corrected for $T = 298.15$ K using the $\Delta_{cr}^g C_{p,m}^o$, calculated as $-(50 \pm 20) \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ according to estimations made by Burkinshaw and Mortimer [20];

TABLE 2
Purification details of phthalide and phthalic anhydride compounds provided by Aldrich Chemical Co.

Chemical Name	CAS Registry No.	Initial molar fraction purity	Purification method	Final massic fraction purity[a]	Analysis method
Phthalide	87-41-2	0.998	Vacuum sublimation	0.9999 ± 0.0002	Gravimetric analysis
Phthalic anhydride	85-44-9	0.994	Vacuum sublimation	0.9999 ± 0.0003	Gravimetric analysis

[a] Results of combustion study based on percentage of carbon dioxide recovery; mean and standard deviation of the mean for seven experiments.