

Experimental study on the thermochemistry of 1-(2*H*)-phthalazinone and phthalhydrazide

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Abstract

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion of 1-(2*H*)-phthalazinone and phthalhydrazide, both in the solid phase, were measured at $T = 298.15$ K by static bomb calorimetry. Further, the standard molar enthalpies of sublimation, at $T = 298.15$ K, of these two phthalazine derivatives were derived from the Knudsen effusion technique. The combustion calorimetry results together with those obtained from the Knudsen effusion technique, were used to derive the standard molar enthalpies of formation, at $T = 298.15$ K, in the gaseous phase for 1-(2*H*)-phthalazinone and phthalhydrazide, respectively as, (79.1 ± 1.8) kJ · mol⁻¹ and $-(107.4 \pm 2.4)$ kJ · mol⁻¹. © 2008 Elsevier Ltd. All rights reserved.

Keywords: Standard molar enthalpy of formation; Standard molar enthalpy of sublimation; Combustion calorimetry; Knudsen effusion technique; 1-(2*H*)-Phthalazinone; Phthalhydrazide

1. Introduction

Nitrogen heterocyclic compounds are a very important class of chemical products as shown by the numerous studies published about their applicability in different areas of knowledge. Among the bicyclic nitrogen heterocycles, phthalazines are an interesting class of compounds with a large range of applications. They are suggested as having vaso relaxant [1], antihypertensive [2], or anti-HIV activities [3]. These compounds are referenced in chemiluminescence studies [4] and they are also used to prepare membranes for several purposes [5,6]. Although their high importance and large applications, the thermochemical data available in the literature for nitrogen heterocycles are still scarce, besides the fact that some of the available data do not have the necessary accuracy. As far as thermochemical data of phthalazine derivatives are concerned, only the phthalazine itself was studied in our laboratory

[7] and no other experimental thermochemical data was found in the literature for this family of compounds.

In order to start to overcome this situation and as part of our interest on the thermochemistry of nitrogen heterocycles, in the present work, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed phase, at $T = 298.15$ K, of 1-(2*H*)-phthalazinone [CAS 119-39-1] and phthalhydrazide [CAS 1445-69-8], whose structural formula is shown in figure 1, were determined from the values of the standard molar energies of combustion. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were derived from the Knudsen effusion technique. From these results, the standard molar enthalpies of formation in the gaseous state, at the temperature 298.15 K, were calculated.

2. Experimental

2.1. Compounds and purity control

The 1-(2*H*)-phthalazinone and phthalhydrazide were obtained commercially from Aldrich Chemical Co., and

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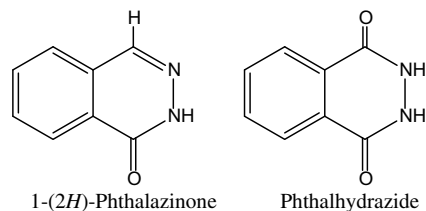


FIGURE 1. Structural formula of 1-(2H)-phthalazinone and of phthalhydrazide.

were purified by repeated sublimations under reduced pressure until the recoveries of the carbon dioxide resulted from combustions were satisfactory. The average ratios

TABLE 1
Areas and transmission probability factors of the effusion orifices

	Orifice number	A_o/mm^2	w_o
		<i>Knudsen-1</i>	
	1	0.6627	0.9899
	2	0.7854	0.9907
	3	0.9958	0.9917
		<i>Knudsen-2</i>	
Small orifices	A1	0.502	0.988
	A2	0.509	0.988
	A3	0.523	0.988
Medium orifices	B4	0.774	0.991
	B5	0.783	0.991
	B6	0.792	0.991
Large orifices	C7	1.019	0.992
	C8	1.125	0.992
	C9	1.131	0.992

TABLE 2
Results of combustion experiments, at $T = 298.15$ K, for 1-(2H)-phthalazinone

Experiment	1	2	3	4	5	6
$m(\text{CO}_2, \text{total})/\text{g}$		2.46196	1.91596			1.97786
$m(\text{cpd})/\text{g}$	0.69742	1.02152	0.79293	0.84691	0.84427	0.81879
$m(\text{fuse})/\text{g}$	0.00346	0.00291	0.00354	0.00324	0.00348	0.00330
$\Delta T_{\text{ad}}/\text{K}$	1.19253	1.74287	1.35478	1.44645	1.44230	1.39930
$e_f/(\text{J} \cdot \text{K}^{-1})$	15.52	16.01	15.76	15.78	15.82	15.77
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U(\text{IBP})^a/\text{J}$	19103.54	27921.14	21703.35	23171.90	23105.52	22416.41
$\Delta U(\text{fuse})/\text{J}$	56.19	47.26	57.49	52.62	56.52	53.59
$\Delta U(\text{HNO}_3)/\text{J}$	50.72	72.18	53.34	56.90	58.27	58.15
$\Delta U(\text{ign})/\text{J}$	1.17	1.05	0.98	1.07	1.02	1.17
$-\Delta U(\text{carbon})/\text{J}$		33.00				
$\Delta U_{\Sigma}/\text{J}$	15.43	23.34	17.75	19.07	18.99	18.35
$-\Delta_c u^\circ/\text{J} \cdot \text{g}^{-1}$	27216.31	27225.47	27208.92	27208.69	27209.00	27218.60
%CO ₂	(100.003)	99.945	100.075	(100.003)	(100.003)	99.957
		$\langle \Delta_c u^\circ \rangle = -(27214.5 \pm 2.8)/(\text{J} \cdot \text{g}^{-1})$				

$m(\text{CO}_2, \text{total})$ is the total mass of carbon dioxide recovered in the combustion; $m(\text{cpd})$ is the mass of compound burnt in each experiment; $m(\text{fuse})$ is the mass of the cotton thread fuse; ΔT_{ad} is the adiabatic temperature rise; e_f is the energy equivalent of the calorimeter including the contents of the bomb in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; $\Delta U(\text{IBP})$ is the energy change for 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 supplied for ignition, $\Delta U(\text{carbon})$ is the energy correction for the carbon residue soot formation; ΔU_{Σ} is the standard state correction; $\Delta_c u^\circ$ is the massic energy of combustion of the compound; %CO₂ is the percentage of the mass of carbon dioxide recovered after each combustion to that calculated from the mass of the sample.

^a $\Delta U(\text{IBP})$ already includes $\Delta U(\text{ign})$.

of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample were: for 1-(2H)-phthalazinone ($100.003 \pm 0.004\%$) and for phthalhydrazide ($99.943 \pm 0.004\%$), where the uncertainties are twice the standard deviation of the mean. The densities of the compounds were determined experimentally as $1.29 \text{ g} \cdot \text{cm}^{-3}$ and $1.39 \text{ g} \cdot \text{cm}^{-3}$ for 1-(2H)-phthalazinone and phthalhydrazide, respectively. The purity of the compounds was also confirmed by g.l.c.

2.2. Combustion calorimetry

The energies of combustion of these two phthalazine derivatives were measured using a static-bomb calorimeter, previously described in the literature [8,9].

Using the same procedure as described in reference [10], the energy equivalent of the calorimeter was determined by combustion of Thermochemical Standard benzoic acid, sample BAS 693976/01, with $\Delta_c u = -(26434.1 \pm 3.5) \text{ J} \cdot \text{g}^{-1}$ [11] under bomb conditions. The energy equivalent of the calorimeter was derived as $\epsilon_{\text{cal}} = (16004.8 \pm 1.6) \text{ J} \cdot \text{K}^{-1}$, as the average of eight combustion experiments with benzoic acid. The results from the calibration were corrected to give the energy equivalents, ϵ_{cal} , corresponding to average mass of water added to the calorimeter: 3119.6 g; the uncertainties quoted are the standard deviations of the mean.

In all combustion experiments, 1.00 cm^3 of water was introduced into the bomb, a twin-valve combustion bomb Type 1108, Parr Instrument Company, with an internal volume of 0.342 cm^3 . The bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

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