Thermochemical Study of Three Hindered Pyridine Derivatives

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The present work reports the values of the gaseous standard ($p° = 0.1$ MPa) molar enthalpy of formation of three pyridine derivatives substituted with one, two, and three *tert*-butyl groups, in positions para, ortho-ortho and ortho-para-ortho to the nitrogen, respectively. The standard molar energies of combustion of each compound, determined by static bomb calorimetry, yielded their standard molar enthalpies of formation in the condensed phase at $T = 298.15$ K, which together with the values of the standard molar enthalpies of vaporization or sublimation, measured by Calvet microcalorimetry, allowed the calculation of the standard gas phase molar enthalpy of formation of each compound studied. The enthalpies of combustion for 4-*tert*-butylpyridine (l), 2,6-di-*tert*-butylpyridine (l) and 2,4,6-tri-*tert*-butylpyridine (cr) were found to be, respectively, $-(5\ 370.1 \pm 3.4)$ kJ mol^{-1}, $-(7954.2 \pm 4.0)$ kJ mol^{-1}, and $-(10\ 542.9 \pm 4.9)$ kJ mol^{-1}. The molar enthalpies of vaporization were measured as (54.4 ± 1.3) kJ mol^{-1} for 4-*tert*-butylpyridine, (56.6 ± 1.2) kJ mol^{-1} for 2,6-di-*tert*-butylpyridine, whereas the enthalpy of sublimation of 2,4,6-tri-*tert*-butylpyridine was found to be (78.3 ± 1.7) kJ mol^{-1}.

Introduction

The molecular structure of an important class of the nitrogen heterocyclic compounds having one sp^2-hybridized nitrogen atom as part of a ring, in addition to sp^2-hybridized carbon results in pyridine, the simplest azabenzene, whose electronic structure is strongly perturbed by the presence of the electronegative nitrogen atom. Although the third sp^2 orbital in each carbon atom is used for the linking with the hydrogen atom, that corresponding orbital for the nitrogen atom contains a pair of electrons in the molecular plane of the ring. Consequently, the more electronegative nitrogen atom compared to the carbon atoms does not donate electronic density to the ring π-system but withdraws electronic density from it, both inductively and by resonance. In fact, the resonance structures of pyridine, combined with the knowledge of the protonic chemical shifts, confirm that the nitrogen atom removes electronic density from the ortho positions, by inductive and resonance effects, whereas only the resonance effect is present at the para position.[1]

Pyridine is a simple and fundamentally important aromatic heterocyclic organic compound and its derivatives are industrially important in applications ranging from the development of new pesticides to the production of new pharmaceutical drug molecules and new products in the petrochemical industry.[2] The breaking and making of chemical bonds involved in chemical processes justifies the need for thermochemical data of key compounds from which it should be possible to predict data for unstudied related compounds.

The systematic study of thermochemical properties of pyridine derivatives, both in the condensed and gaseous phases, is one of the subjects of our research work. For several years we have studied the thermochemical properties of various pyridine compounds in order to establish how the transferability of bond energy contributions applies to these compounds[3–17] and, consequently, to correlate their behavior in terms of energetics, structure and reactivity. In addition we have been examining the effect of different substituents on the dissociation enthalpy of the (N−O) bond of the nitrogen N-oxide heterocycles, a study that requires the knowledge of thermochemical data of the correspondent heterocycles not having the (N−O) bond.[18]

This work is a study of the effects of the bulky *tert*-butyl substituents on the pyridinic ring and reports the calorimetric study of the three compounds, represented in figure 1: the liquids 4-*tert*-butylpyridine (4tBuPy) and 2,6-di-*tert*-butylpyridine (2,6dtBuPy) and the solid 2,4,6-tri-*tert*-butylpyridine (2,4,6ttBuPy). The standard molar enthalpies of formation in the gaseous state of the three pyridine derivatives were derived from their standard molar energies of combustion, measured by static bomb calorimetry, and the correspondent standard molar enthalpies of vaporization or sublimation, measured by Calvet microcalorimetry.

These hindered substituted pyridine derivatives have received a large attention due their relevant applications; the monossubstituted compound has been widely used as an additive in the electrolyte solution of a new class of low-cost photovoltaic cells, called Grätzel cells,[19–24] and the disubstituted compound is used in the production of homopolymers, copolymers or block copolymers.[25] Available information regarding 2,4,6-tri-*tert*-butylpyridine is scarce probably due to the instability of this compound whose storage and handling requires an inert atmosphere.[26]

Experimental Section

Purification of the Samples. The compounds 4-*tert*-butylpyridine (purity 99 %, CAS 3978-81-2) and 2,6-di-*tert*-butylpyridine (purity 98.5 %, CAS 585−48−8) were obtained commercially from Sigma-Aldrich. Both compounds were purified by repeated fractional distillation over KOH, under reduced pressure (boiling points, respectively, 338 K at $p = 1$ kPa and

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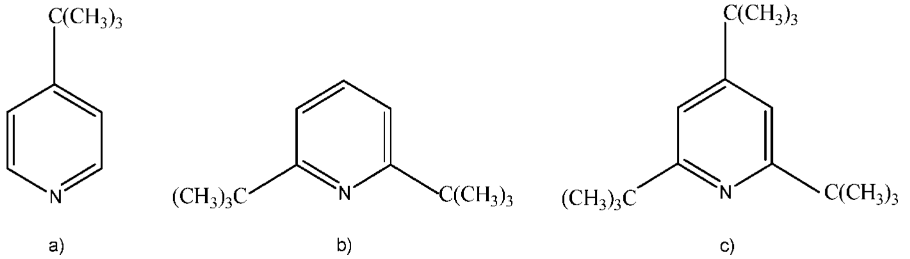

Figure 1. Molecular structures for (a) 4-*tert*-butylpyridine; (b) 2,6-di-*tert*-butylpyridine; (c) 2,4,6-tri-*tert*-butylpyridine.

359 K at $p = 1.5$ kPa), their purities being checked by glc (using an HP 4890 apparatus with a column HP-5, 5 % diphenyl and 95 % dimethylpolysiloxane, under a nitrogen pressure of 21 kPa, and the temperature of the oven 423 K) and also by the percentage of CO_2 recovered in the combustion experiments; molar fraction purity 0.999.

2,4,6-Tri-*tert*-butylpyridine (purity 99.2 %, CAS 20336-15-6) was obtained commercially also from Sigma-Aldrich. The compound has been submitted to additional purification, by sublimation under reduced pressure, immediately before the calorimetric measurements. The melting point measured in a melting point apparatus, Stuart Scientific SMP2, is 340 K to 342 K. The DSC thermogram did not show any phase transitions before the melting temperature; molar fraction purity 0.998.

The average ratios of the mass of carbon dioxide recovered to that calculated from the mass of sample, together with the standard deviation of the mean, were 4tBuPy, (1.0001 ± 0.0004); 2,6dtBuPy, (0.9997 ± 0.0003); 2,4,6ttBuPy, (1.0004 ± 0.0005). The densities of the samples are 4tBuPy, $\rho = 0.915$ $g\cdot cm^{-3}$;[26] 2,6dtBuPy, $\rho = 0.852$ $g\cdot cm^{-3}$;[26] and that of 2,4,6ttBuPy (estimated from the weight and volume of a pellet), $\rho = 1.09$ $g\cdot cm^{-3}$.

Static Bomb Calorimetry. The massic energies of combustion of the compounds were measured using a static bomb calorimeter equipped with a twin valve bomb of internal volume of 0.290 dm^3, previously described.[27–29]

The calorimetric system was calibrated using benzoic acid (NBS Standard Reference Material 39j) with a massic energy of combustion under standard bomb conditions of $-(26434 \pm 3)$ $J\cdot g^{-1}$. The calibration results were corrected to give the energy equivalent ε(cal) corresponding to the average mass of water added to the calorimeter, 2900.0 g. Calibration experiments were made in oxygen at $p = 3.04$ MPa, with 1.00 cm^3 of deionized water added to the bomb, leading to the values of the energy equivalent of the calorimeter, ε(cal) $= (15553.3 \pm 0.9)$ $J\cdot K^{-1}$ for the study of 4tBuPy and ε(cal) $= (15546.3 \pm 1.3)$ $J\cdot K^{-1}$ for the study of 2,6dtBuPy and 2,4,6ttBuPy; the uncertainties quoted are the standard deviations of the mean.

The compounds were enclosed in polyester bags made of Melinex, [$\Delta_c u° = -(22902 \pm 5$ $J\cdot g^{-1}$), a value confirmed by combustion of Melinex samples in our laboratory], using the technique described by Skinner and Snelson.[30] The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported.[30] The samples were ignited at $T = (298.150 \pm 0.001)$ K in oxygen at $p = 3.04$ MPa with 1.00 cm^3 of deionized water added to the bomb. The electrical energy for ignition ΔU(ign) was determined from the change in potential difference across a 1400 μF condenser when discharged through the platinum ignition wire. Temperature measurements were automatically collected every ten seconds and the initial temperature of the combustion experiments was 298.15 K to which the energy of reaction was always referred. The combustion products were analyzed after the calorimetric measurements; the carbon dioxide was collected in absorption tubes and the amount of nitric acid determined by titration. The corrections for nitric acid formation were based on -59.7 $kJ\cdot g^{-1}$ for the molar energy of formation of 0.1 $mol\cdot dm^{-3}$ HNO_3 (aq) from N_2 (g), O_2 (g) and H_2O (l).[31] For the cotton thread fuse, $-\Delta_c u° = 16250$ $J\cdot g^{-1}$,[32] a value previously confirmed in our laboratory. The values for the pressure coefficient of specific energy, $(\partial u/\partial p)_T$, were assumed to be -0.2 $J\cdot g^{-1}\cdot MPa^{-1}$ at $T = 298.15$ K, typical values for most organic compounds.[33]

The mass of compound, m(compound), 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 Melinex. The standard massic energy of combustion, $\Delta_c u°$, was calculated by the procedure given by Hubbard et al.[34]

Calvet Microcalorimetry. The enthalpies of vaporization were determined in a Calvet high temperature microcalorimeter (SETARAM HT1000D), using a technique previously described[35] identical to that described for the measurements of enthalpies of sublimation, the "vacuum-sublimation drop microcalorimetric method".[36] The liquid samples of about 6 mg to 9 mg in a thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in the microcalorimeter, held at $T = 365$ K and $T = 324$ K, for 4tBuPy and 2,6dtBuPy, respectively, and then removed from the hot zone by vacuum vaporization. The enthalpy of sublimation of 2,4,6ttBuPy was measured at $T = 329$ K. The thermal corrections for the glass capillary tubes were evaluated and reduced in each run, by dropping empty tubes of nearly equal mass, on both calorimeter cells; $\Delta^{T}_{298.15\ K}H^{o}_{m}(g)$ was estimated by a group method based on the values of Stull et al.[37] The microcalorimeter was calibrated in situ using the reported standard molar enthalpies of vaporization for decane[38] and of sublimation for naphthalene.[39]

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission.[40]

Results

The results for a typical individual combustion experiment of each compound are given in Table 1, where Δm (H_2O) is the deviation of the mass of water added to the calorimeter from 2900.0 g, the mass assigned for ε(cal); ΔU_{Σ} is the correction to the standard state; $c_p(H_2O, l)$ is the heat capacity of liquid water, ε_f is the energy of the bomb contents after ignition, ΔT_{ad} is the temperature rise, corrected for heat exchange and the energy of stirring, and ΔU_{ign} is the energy associated with the ignition. The solid and liquid samples were ignited at $T = 298.15$ K and

Table 1. Typical Combustion Experiments at $T = 298.15$ K

	4tBuPy	2,6dtBuPy	2,4,6ttBuPy
$m(CO_2, \text{total})/\text{g}$	1.23479	1.27768	1.27098
$m(\text{compound})/\text{g}$	0.37832	0.38590	0.36176
$m(\text{Melinex})/\text{g}$	0.05402	0.05281	0.07555
$m(\text{fuse})/\text{g}$	0.00172	0.00168	0.00250
$\Delta T_{ad}/\text{K}$	1.04754	1.11068	1.10470
$\varepsilon_f/(\text{JK}^{-1})$	14.34	14.56	13.49
$\Delta m(H_2O)/\text{g}$	−1.4	+0.7	−0.3
$-\Delta U(\text{IBP})^a/\text{J}$	16300.67	17285.77	17186.88
$\Delta U(\text{Melinex})/\text{J}$	1237.27	1209.40	1730.26
$\Delta U(\text{fuse})/\text{J}$	27.93	27.28	40.60
$\Delta U(HNO_3)/\text{J}$	23.53	10.46	17.47
$\Delta U(\text{ign})/\text{J}$	0.92	0.62	0.63
$-\Delta U_\Sigma/\text{J}$	7.62	7.18	6.13
$-\Delta_c u°/(\text{J}\cdot\text{g}^{-1})$	39660.39	41519.69	42548.71

[a] ΔU(IBP) includes ΔU(ign).

Table 2. Individual Values of the Massic Energy of Combustion, $\Delta_c u°$, at $T = 298.15$ K

4tBuPy	2,6dtBuPy	2,4,6ttBuPy
39 688.40	41 482.62	42 530.89
39 700.58	41 496.37	42 548.71
39 694.02	41 527.47	42 528.58
39 620.73	41 522.89	42 538.60
39 660.39	41 519.69	42571.04
39 648.36	41 538.09	
39 658.70		
	$-<\Delta_c u°>^a/(\text{J}\cdot\text{g}^{-1})$	
39 667 ± 12	41514.5 ± 8.5	42 543.4 ± 7.7

[a] Mean values and standard deviation of the mean.

Table 3. Derived Standard ($p° = 0.1$ MPa) Molar Values in the Liquid or Crystalline Phases at $T = 298.15$ K[a]

compound	$\Delta_c U^o_m(\text{cr,l})$/ kJ·mol^{-1}	$\Delta_c H^o_m(\text{cr,l})$/ kJ·mol^{-1}	$\Delta_f H^o_m(\text{cr,l})$/ kJ·mol^{-1}
4tBuPy (l)	−5 363.3 ± 3.4	−5 370.1 ± 3.4	−29.4 ± 3.6
2,6dtBuPy (l)	−7 942.4 ± 4.0	−7 954.2 ± 4.0	−162.7 ± 4.4
2,4,6ttBuPy (cr)	−10 526.2 ± 4.9	−10 542.9 ± 4.9	−291.2 ± 5.4

[a] The uncertainties are twice the overall standard deviation of the mean (level of confidence 95%).

the energy associated to the isothermal bomb process, ΔU (IBP), was calculated from eq 1, according to ref 34.

$$\Delta U(\text{IBP}) = -\{\varepsilon_{cal} + \Delta m(H_2O)c_p(H_2O, \text{l}) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\text{ign}) \quad (1)$$

The individual results of all combustion experiments, 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 and enthalpies of combustion, $\Delta_c U^o_m(\text{l, cr})$ and $\Delta_c H^o_m(\text{l, cr})$, respectively and the standard molar enthalpies of formation for the compounds in the condensed phase, $\Delta_f H^o_m(\text{l, cr})$, at $T = 298.15$ K. In accordance with the normal thermochemical practice,[41] 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 and in the values of auxiliary quantities. To derive $\Delta_f H^o_m(\text{l, cr})$ from $\Delta_c H^o_m(\text{l, cr})$ the standard molar enthalpies of formation of H_2O (l) and CO_2 (g), at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ·mol^{-1}[42] and $-(393.51 \pm 0.13)$ kJ·mol^{-1},[42] respectively, were used.

Measurements of the standard molar enthalpies of vaporization, $\Delta^g_l H^o_m$, or sublimation, $\Delta^g_{cr} H^o_m$, at $T = 298.15$ K are given in Table 4 with uncertainties of twice the standard deviation of the mean. The derived standard molar enthalpies of formation, in both the condensed and gaseous phases, for the three studied compounds, are summarized in Table 5.

Table 4. Calorimetric Values for the Standard ($p° = 0.1$ MPa) Molar Enthalpies of Sublimation and Vaporization at $T = 298.15$ K[a]

compound	no. of expts	T/K	$\Delta^{g,T}_{cr,l,298.15K} H^o_m$/ kJ·mol^{-1}	$\Delta^T_{298.15K} H^o_m(g)$/ kJ·mol^{-1}	$\Delta^g_{cr,l} H^o_m$ ($T = 298.15$K)/ kJ·mol^{-1}
4tBuPy (l)	7	365	67.1 ± 1.3	12.7	54.4 ± 1.3
2,6dtBuPy (l)	7	324	64.0 ± 1.2	7.4	56.6 ± 1.2
2,4,6ttBuPy (cr)	6	329	90.2 ± 1.7	11.9	78.3 ± 1.7

[a] The uncertainties are twice the overall standard deviation of the mean (level of confidence 95%).

Table 5. Derived Standard ($p° = 0.1$ MPa) Molar Enthalpies of Formation at $T = 298.15$ K[a]

compound	$\Delta_f H^o_m(\text{cr,l})$/ kJ.mol^{-1}	$\Delta^g_{cr,l} H^o_m$/ kJ.mol^{-1}	$\Delta_f H^o_m(g)$/ kJ·mol^{-1}
4tBuPy (l)	−29.4 ± 3.6	54.4 ± 1.3	25.0 ± 3.8
2,6dtBuPy (l)	−162.7 ± 4.4	56.6 ± 1.2	−105.5 ± 4.6
2,4,6ttBuPy (cr)	−291.2 ± 5.4	78.3 ± 1.7	−211.4 ± 5.7

[a] The uncertainties are twice the overall standard deviation of the mean (level of confidence 95%).

Table 6. Comparison of Values of Enthalpy of Formation in the Gaseous State at $T = 298$ K Measured in This Work with Literature Values

compound	$\Delta_f H^o_m(g)$/kJ·mol^{-1}	δ-increment/kJ·mol^{-1}
Py	140.4 ± 0.7 [43]	
4tBuPy	25.0 ± 3.8[a]	−115.4 ± 3.9
2,6dtBuPy	−105.5 ± 4.6[a]	−245.9 ± 4.7
2,4,6ttBuPy	−211.4 ± 5.7[a]	−351.8 ± 5.7
4MePy	104.0 ± 0.9[43]	−36.4 ± 1.1
2,6dMePy	58.1 ± 1.5[43]	−82.3 ± 1.7
2,4,6 tMePy	19.3 ± 2.4[6]	−121.1 ± 2.5

[a] This work.

Discussion

The energetic contributions associated with the substitution of *tert*-butyl (tBu) groups on positions 4-,2,6- and 2,4,6- of the basic structure (pyridine, Py) can be evaluated from the results obtained in this work and compared with the corresponding effects observed for identical substitutions of methyl (Me) groups. Table 6 contains all the necessary literature values, together with the results obtained in the present study, and lists the enthalpic increment, δ, to the standard molar enthalpies of formation in the gaseous state for the substitution of one, two, and three (X = Me or tBu) groups into the pyridine ring (Py).

$$\delta\text{-increment} = \Delta_f H^o_m(X_n\text{Py, g}) - \Delta_f H^o_m(\text{Py, g}) \qquad n = 1, 2, \text{or } 3 \quad (2)$$

The effect of both alkyl substituents in the ortho and para positions on the gas phase enthalpies of formation is that both substituents increase the stability of the molecule relative to hydrogen. Ribeiro da Silva[3] showed in terms of increments and within the experimental uncertainty that the enthalpy of formation of gaseous 2,4,6-trimethylpyridine (2,4,6tMePy) could be obtained from the value of the enthalpy of formation of gaseous pyridine, adding the enthalpic increments for 4-methylpyridine (4MePy) and 2,6-dimethylpyridine (2,6dMePy) relatively to pyridine. For the *tert*-butyl compounds studied in the present work, identical treatment leads to the value $-(220.9 \pm 6.1)$ kJ mol^{-1} for the enthalpy of formation of gaseous 2,4,6-tri-*tert*-butylpyridine. Although the experimental value $-(211.4 \pm 5.7)$ kJ mol^{-1} is close to the estimated value, it points to a relative instability of the 2,4,6ttBuPy molecule that can be explained by the steric effects of the two hindered substituents adjacent to the nitrogen atom, since the steric requirement of the *tert*-

butyl groups are such that substituents at the positions 2 and 6 are incapable of achieving a conformation which minimizes stereochemical interactions.

Our conclusion is enforced by the studies of other researchers[44,45] since the compound 2,6-di-*tert*-butylpyridine exhibits unusual reduced basicity, even being mentioned as a nonnucleophilic base. An explanation proposed for this feature is the fact that there is a stereochemical barrier which hinders the addition of the proton to the basic center.

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