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Thermodynamic Properties of Three Pyridine Carboxylic Acid Methyl Ester Isomers

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The present work reports the values of the standard ($p° = 0.1$ MPa) molar energies of combustion for the liquid isomers methyl picolinate and methyl isonicotinate and for the crystalline isomer methyl nicotinate measured by static bomb calorimetry. The molar enthalpies of vaporization of the three isomers at $T = 298.15$ K as well as the molar enthalpies of sublimation of two of them (methyl picolinate and methyl nicotinate) were derived from vapor pressure measurements at different temperatures using a static method. The molar enthalpies of vaporization at $T = 298.15$ K of methyl picolinate and methyl isonicotinate were also measured using Calvet microcalorimetry. The thermal behavior of the compounds was studied by differential scanning calorimetry, and the temperatures and the molar enthalpies of fusion were determined using this technique. The experimental results were used to derive the gaseous standard molar enthalpies of formation, at 298.15 K, of the three pyridinecarboxylic acid methyl ester isomers and the triple points of the ortho and meta isomers.

Introduction

Thermochemical data are essential for the understanding of the relations between the structure and reactivity of molecules, and that reason justifies the importance of the study of key compounds from several classes of compounds because such data permit clarification of the chemical behavior of the corresponding species. In this context, systematic experimental and theoretical thermochemical studies on heterocyclic molecules derived from pyridine have been done in our Thermochemistry Laboratory for more than a decade in order to evaluate the energetic effects of different substituents on the pyridinic ring.[1−14] The main goal of the present work is to determine the gaseous enthalpies of formation of methyl picolinate (2-PyCOOCH$_3$), methyl nicotinate (3-PyCOOCH$_3$), and methyl isonicotinate (4-PyCOOCH$_3$), represented in Figure 1, together with the measurement of other relevant properties to the thermodynamic characterization of those isomers.

The present work reports for the three pyridinecarboxylic acid methyl ester isomers the experimental values of the standard molar energies of combustion, the standard molar enthalpies of vaporization, and the standard molar enthalpies of sublimation of two of them—methyl picolinate and methyl nicotinate. For methyl isonicotinate, the enthalpy of sublimation was estimated from the enthalpies of fusion and of vaporization.

The experimental results are used to derive the gaseous standard molar enthalpies of formation, at $T = 298.15$ K, of the three pyridinecarboxylic acid methyl ester isomers. In order to complement the results, the thermal behavior of the compounds was studied, and the temperatures and the molar enthalpies of fusion were determined by differential scanning calorimetry.

Experimental Section

Materials. The compound 2-PyCOOCH$_3$ (CASRN 2459-07-6) was a commercial sample from Aldrich, 99 %. The isomers 3-PyCOOCH$_3$ (CASRN 93-60-7) and 4-PyCOOCH$_3$ (CASRN 2459-09-8) were prepared by the esterification of nicotinic acid and isonicotinic acid, respectively, with trimethylorthoacetate according to the published synthetic method of Trujillo and Gopalan.[15] Both products were collected and further purified by fractional distillation under reduced pressure. The purities of 2-PyCOOCH$_3$ and 4-PyCOOCH$_3$ were checked by GLC (using an HP 4890 apparatus with a 15 m length column HP-5, 5 % diphenyl, and 95 % dimethylpolysiloxane under a nitrogen pressure of 21 kPa; the temperature oven was 423 K), whereas the purity of 3-PyCOOCH$_3$ was confirmed by DSC after it has been dried at $T = 303$ K under reduced pressure. For 3-PyCOOCH$_3$ and for 4-PyCOOCH$_3$, microanalytical determinations yielded the following results (mass fractions). For 3-PyCOOCH$_3$: C$_7$H$_7$NO$_2$, C, 0.6139; H, 0.0516; N, 0.1011. For 4-PyCOOCH$_3$: C$_7$H$_7$NO$_2$, C, 0.6137; H, 0.0507; N, 0.1013. Calcd C, 0.6131; H, 0.0514; N, 0.1021. The percentage of CO$_2$ recovered in the combustion experiments also showed the high purity of the samples.

The densities (ρ) of the samples and the average ratios (μ) of the mass of carbon dioxide recovered to that calculated from the mass of sample, together with the standard deviation of the mean, were as follows: 2-PyCOOCH$_3$, $\rho = 1.137$ g·cm^{-3},[16] $\mu = (0.9999 \pm 0.0003)$; 3-PyCOOCH$_3$, $\rho = 1{,}0$ g·cm^{-3} (assumed),

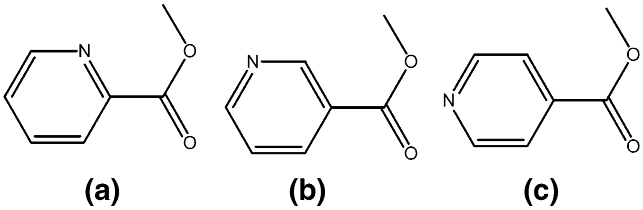

Figure 1. Molecular formulas for pyridinecarboxylic acid methyl ester isomers: (a) methyl picolinate, (b) methyl nicotinate, and (c) methyl isonicotinate

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$\mu = (0.9998 \pm 0.0003)$; 4-$PyCOOCH_3$, $\rho = 1.161\ g\cdot cm^{-3}$,[16] $\mu = (0.9980 \pm 0.0005)$.

Calorimetric Measurements

Static Bomb Calorimetry. The energies of combustion of the three compounds were determined using an isoperibol static bomb calorimeter, with a twin valve bomb of internal volume 0.290 dm^3. The calorimeter and technique have been previously described.[17−19] The energy equivalent of the calorimeter was determined twice during this experimental study, by the combustion in oxygen of thermochemical standard benzoic acid NBS, SRM 39j, with the massic energy of combustion of $\Delta_c u = -(26434 \pm 3)\ J\cdot g^{-1}$ (value under certificate conditions). 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. For the study of isomers 3-$PyCOOCH_3$ and 4-$PyCOOCH_3$, one set of 12 calibration experiments was made in oxygen at $p = 3.04$ MPa with 1.00 cm^3 of water added to the bomb and yielded $\epsilon_{cal} = (15546.5 \pm 1.1)\ J\cdot K^{-1}$, where the uncertainty quoted is the standard deviation of the mean. For the study of 2-$PyCOOCH_3$, another set of 11 calibration experiments was made, yielding $\epsilon_{cal} = (15553.3 \pm 0.9)\ J\cdot K^{-1}$. For the combustion experiments, crystalline 3-$PyCOOCH_3$ was burnt in pellet form whereas the liquids 2-$PyCOOCH_3$ and 4-$PyCOOCH_3$ were enclosed in melinex bags, according to the technique described by Skinner and Snelson.[20] The massic energy of combustion of dry melinex, $\Delta_c u^\circ = -(22902 \pm 5)\ J\cdot g^{-1}$,[20] was confirmed by combustion of melinex samples in our laboratory. The mass of melinex used in each experiment was corrected for the mass fraction of water (0.0032).[20] All 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 previously added to the bomb.

The electrical energy for ignition ΔU(ign.) was determined from the change in potential difference across a 1400 μF capacitor when discharged through the platinum ignition wire. For the cotton thread fuse, of empirical formula $CH_{1.686}O_{0.843}$, the massic energy of combustion is $\Delta_c u^\circ = -16250\ J\cdot g^{-1}$.[21] The corrections for nitric acid formation, $\Delta U(HNO_3)$, were based on the value $-59.7\ kJ\cdot mol^{-1}$,[22] for the molar energy of formation of 0.1 $mol\cdot dm^{-3}$ HNO_3(aq) from N_2, O_2, and H_2O(l). An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2\ J\cdot g^{-1}\cdot MPa^{-1}$ at $T = 298.15$ K, a typical value for most organic compounds,[23] was assumed. The mass of compound, m(compound), used in each experiment was determined from the total mass of carbon dioxide, $m(CO_2$, total), produced after allowance for that formed from the cotton thread fuse and melinex. For each compound, the standard massic energy of combustion ($\Delta_c u^\circ$) was calculated by the procedure given by Hubbard et al.[24]

Calvet Microcalorimetry. The enthalpies of vaporization of 2-$PyCOOCH_3$ and 4-$PyCOOCH_3$ were determined in a Calvet high-temperature microcalorimeter (SETARAM HT 1000), using the "vacuum-sublimation drop microcalorimetric method",[25] adapted for liquids.[26] Samples about (6 to 9) mg of the liquid compounds, contained in a thin glass capillary tube sealed at one end, were dropped at room temperature into the hot reaction vessel of a high-temperature Calvet microcalorimeter held at $T = 386$ K for 2-$PyCOOCH_3$ or at $T = 388$ K for 4-$PyCOOCH_3$ and then removed from the hot zone by vacuum evaporation. The observed enthalpies of vaporization, $\Delta_{l,298.15K}^{g,T}H_m^o$, were corrected to $T = 298.15$ K, using $\Delta_{298.15K}^{T}H_m^o$(g) estimated by a group method based on the values of Stull et al.[27] The microcalorimeter was calibrated in situ using the reported standard molar enthalpies of sublimation of naphthalene[28] and of vaporization of n-decane.[29] The determination of the enthalpy of sublimation of the 3-$PyCOOCH_3$ isomer has not been performed using Calvet microcalorimetry because its low temperature of fusion and high vapor pressure did not allow the accurate use of this technique.

Differential Scanning Calorimetry. Enthalpies and temperatures of fusion of the three isomers were determined with a Setaram DSC 141 calorimeter. Thermograms of samples hermetically sealed in steel pans were recorded in an air atmosphere at a scanning rate of 0.017 $K\cdot s^{-1}$. All the pans were weighed before and after the experiments to confirm that no product leakage had occurred. A Mettler UMT2 microbalance, with a sensitivity of (1×10^{-7}) g, has been used.

For each compound, at least five samples weighing (8 to 10) mg were recorded. To verify the stability of each compound after melting, several scans were performed for each sample. Both the cooling and heating scans were reproducible after several cycles for the three isomers. The samples were studied over the following temperature ranges: (253 to 303) K for 2-$PyCOOCH_3$, (293 to 323) K for 3-$PyCOOCH_3$, and (263 to 303) K for 4-$PyCOOCH_3$. No solid−solid-phase transitions were observed for the three isomers over these temperature intervals.

The cooling scans from above the melting temperature of each compound toward the lower temperature limits were achieved using circulating water from a thermostatic bath for the study of 3-$PyCOOCH_3$ and using circulating dry air, refrigerated with liquid nitrogen, for the study of 2-$PyCOOCH_3$ and of 4-$PyCOOCH_3$. In both cases, an approximately constant cooling rate of 0.017 $K\cdot s^{-1}$ was attained. Each melting curve allowed computing the temperature and enthalpy of fusion of the samples. The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission.[30]

Vapor Pressure Measurements. The vapor pressures of the three isomers were measured at different temperatures using a static apparatus based on a capacitance diaphragm gage. The apparatus and the measuring procedure have been recently described in detail,[31] so only a short description is given here. It is constructed of stainless steel tubing of internal diameter 17 mm with connections ConFlat DN 16 CF and includes all metal angle valves, VAT series 57 high-temperature range for UHV, operated pneumatically. The pressure is measured by a capacitance diaphragm absolute gage MKS Baratron 631A01-TBEH, with a measuring upper limit of 133 Pa and the uncertainty of 0.25 % of the reading pressure, as stated by the manufacturer. The temperature of the pressure sensor is kept at $T = 423$ K by the self-controlling temperature system. The pressure gage has been calibrated at 423 K by the manufacturer at seven equally spaced pressures from 0 to 133 Pa with a maximum deviation of 0.23 %. This calibration is traceable to the National Institute of Standards and Technology (NIST).

The temperature of the sample is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four-wire connection), which is in a good thermal contact with the sample. This thermometer was calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187A). The uncertainty of the temperature measurements is estimated to be better than ± 0.01 K. All temperatures reported here are based on the international temperature scale ITS-90.

The apparatus has been tested by measurements of vapor pressure of recommended reference materials (naphthalene, benzoic acid, benzophenone, and ferrocene) and proved to provide reliable vapor pressure data as well as enthalpies of sublimation or vaporization. The uncertainty in the pressure

Table 1. Typical Combustion Experiments at T = 298.15 K[a]

	2-$PyCOOCH_3$	3-$PyCOOCH_3$	4-$PyCOOCH_3$
$m(CO_2$, total)/g	1.81149	1.40994	1.96846
m(compound)/g	0.75391	0.62594	0.81060
m(melinex)/g	0.05002		0.06263
m(fuse)/g	0.00206	0.00236	0.00252
ΔT_{ad}/K	1.30925	1.02071	1.41952
$\epsilon_f/(J\cdot K^{-1})$	14.50	14.20	14.72
$\Delta m(H_2O)$/g	−0.8	−0.3	−2.1
$-\Delta U(IBP)^b$/J	20377.73	15881.65	22076.96
$-\Delta U$(Melinex)/J	1145.66		1434.42
$-\Delta U$(fuse)/J	33.45	38.33	40.92
$-\Delta U(HNO_3)$/J	42.17	31.76	37.13
ΔU(ign.)/J	0.67	1.19	1.18
$-\Delta U_\Sigma$/J	15.57	11.86	17.23
$-\Delta_c u°/(J\cdot g^{-1})$	25387.88	25239.59	25346.81

[a] $m(CO_2$, total) is the total mass of CO_2 formed in the experiment. m(compound) is the mass of compound burnt in the experiment. m(fuse) is the mass of fuse (cotton) used in the experiment. ΔT_{ad} is the corrected temperature rise. ϵ_f is the energy equivalent of contents in the final state. $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 2900.0 g. ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions. ΔU(melinex) is the energy of combustion of melinex. ΔU(fuse) is the energy of combustion of the fuse (cotton). $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation. ΔU(ign.) is the energy of ignition. ΔU_Σ is the energy correction to the standard state. $\Delta_c u°$ is the standard massic energy of combustion. [b] ΔU(IBP) includes ΔU(ign.).

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

2-$PyCOOCH_3$	3-$PyCOOCH_3$	4-$PyCOOCH_3$
25380.38	25221.54	25357.83
25375.17	25216.61	25346.13
25376.34	25253.93	25324.35
25413.21	25218.28	25356.39
25385.84	25235.93	25351.23
25387.88	25239.59	25346.81
	$-\langle\Delta_c u°\rangle/(J\cdot g^{-1})$	
25386.5 ± 5.7	25231.0 ± 6.0	25347.1 ± 5.0

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

compound	$\Delta_c U_m^\circ$(cr, l)	$\Delta_c H_m^\circ$(cr, l)	$\Delta_f H_m^\circ$(cr, l)
2-$PyCOOCH_3$(l)	−3481.5 ± 1.6	−3482.1 ± 1.6	−272.9 ± 1.8
3-$PyCOOCH_3$(cr)	−3460.1 ± 1.8	−3460.7 ± 1.8	−294.2 ± 2.0
4-$PyCOOCH_3$(l)	−3476.0 ± 1.5	−3476.6 ± 1.5	−278.3 ± 1.8

[a] Values in kJ·mol−1.

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

compound	no. of expts	$\frac{T}{K}$	$\frac{\Delta_{l,298.15K}^{g,T} H_m^\circ}{kJ\cdot mol^{-1}}$	$\frac{\Delta_{298.15K}^{T} H_m^\circ(g)}{kJ\cdot mol^{-1}}$	$\frac{\Delta_l^g H_m^{\circ\,(298.15\,K)}}{kJ\cdot mol^{-1}}$
2-$PyCOOCH_3$	6	386	78.3 ± 1.8	11.3	67.0 ± 1.8
4- $PyCOOCH_3$	7	388	79.2 ± 1.4	13.8	65.4 ± 1.4

Table 5. Temperatures and Enthalpies of Fusion of 2-$PyCOOCH_3$, 3-$PyCOOCH_3$, and 4-$PyCOOCH_3$

	calorimetric		indirect method (vapor pressures)		
compound	$\frac{T_{fus}}{K}$	$\frac{\Delta_{cr}^{l} H_m(T_{fus})}{kJ\cdot mol^{-1}}$	$\frac{\Delta_{cr}^{l} H_m(T_{Tr})}{kJ\cdot mol^{-1}}$	$\frac{T_{Tr}}{K}$	$\frac{p_{Tr}}{Pa}$
2-$PyCOOCH_3$	289.2 ± 0.2	16.8 ± 0.1	17.5 ± 0.3	293.4	3.68
3-$PyCOOCH_3$	312.6 ± 0.1	19.3 ± 0.3	19.7 ± 0.2	312.7	56.4
4-$PyCOOCH_3$	283.4 ± 0.4	14.6 ± 0.3			

measurements is adequately described by the equation $\sigma(p/Pa) = 0.01 + 0.0025(p/Pa)$, and the workable temperature and pressure ranges are (243 to 413) K and (0.4 to 133) Pa, respectively.

Results and Discussion

The results for a typical combustion experiment of each one of the three compounds are given in Table 1. In this table, $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the mass assigned for ϵ(cal), 2900.0 g; ΔU_Σ is the correction to the standard state; 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 $\Delta U_{ign.}$ is the energy of ignition. The samples were ignited at T = 298.15 K, and the energy associated to the isothermal bomb process, ΔU (IBP), was calculated from eq 1,[24] where $c_p(H_2O, l)$ is the heat capacity of liquid water:

$$\Delta U(\mathrm{IBP}) = -\{\epsilon_{cal} + \Delta m(\mathrm{H_2O})c_p(\mathrm{H_2O, l}) + \epsilon_f\}\Delta T_{ad} + \Delta U(\mathrm{ign.}) \quad (1)$$

The individual results of all combustion experiments, together with the mean value and its standard deviation of the mean, are given for each compound in Table 2. Table 3 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U_m^\circ$(cr,l) and $\Delta_c H_m^\circ$(cr,l), respectively, and the standard molar enthalpies of formation of the compounds in the condensed phase, $\Delta_f H_m^\circ$(cr,l), at T = 298.15 K. In accordance to the normal thermochemical practice,[32] 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 $\Delta_f H_m^\circ$(cr,l) from $\Delta_c H_m^\circ$(cr,l) the standard molar enthalpies of formation of H_2O(l) and of CO_2(g) at T = 298.15 K, −(285.830 ± 0.042) kJ·mol−1,[33] and −(393.51 ± 0.13) kJ·mol−1,[33] respectively, were used. Values of the standard molar enthalpies of vaporization, $\Delta_l^g H_m^\circ$, at T = 298.15 K, measured using Calvet microcalorimetry, are given in Table 4, where the assigned uncertainties are twice the standard deviation of the mean.

The fusion temperatures were taken as DSC onset temperatures. For each fusion peak, six integrations were performed in order to get the enthalpy of fusion. Table 5 displays the results obtained for each compound. There, the uncertainty associated to each calorimetric result represents twice the standard deviation of the mean of at least six results.

The vapor pressures of 2-$PyCOOCH_3$ and 3-$PyCOOCH_3$ were measured above the crystalline as well as above the liquid phase. The supercooling of both liquids allowed measurements at the same temperature on both the crystalline and the metastable liquid phase over temperature intervals greater than 10 K. The vapor pressures of 4-$PyCOOCH_3$ were measured only above the liquid phase. The experimental results of the vapor pressures listed in Tables 6 to 8 were fitted by the Clarke and Glew equation (eq 2):

$$R\ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_{cd}^{g}G_m^0(\theta)}{\theta} + \Delta_{cd}^{g}H_m^0(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{cd}^{g}C_{p,m}^0(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (2)$$

where p is the vapor pressure, p^0 is a selected reference pressure (in this work we took $p^0 = 10^5$ Pa), θ is a selected reference temperature (in this work we took θ = 298.15 K), R is the molar gas constant (R = 8.314472 J·K−1·mol−1), $\Delta_{cd}^{g}G_m^0$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phase) at the selected

Table 6. Experimental Data on Vapor Pressures of 2-PyCOOCH$_3$[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
	Crystalline			Liquid	
278.20	0.582	0.001	293.12	3.570	−0.012
278.20	0.580	−0.001	293.13	3.566	−0.019
280.68	0.794	−0.003	298.15	5.628	0.038
280.67	0.793	−0.003	298.15	5.601	0.011
283.16	1.086	0.000	303.15	8.522	−0.026
283.15	1.087	0.002	303.15	8.506	−0.042
285.65	1.476	0.003	308.08	12.80	0.01
285.65	1.472	−0.001	308.11	12.79	−0.03
288.14	1.988	0.001	313.12	19.19	0.19
288.15	1.989	−0.001	313.13	19.16	0.15
290.65	2.682	0.010	318.09	27.71	0.06
290.63	2.681	0.015	318.09	27.63	−0.02
		Liquid			
273.21	0.510	0.003	323.05	39.68	0.01
273.21	0.505	−0.002	328.04	56.28	0.02
278.18	0.860	0.008	328.04	56.32	0.06
278.18	0.856	0.004	333.01	78.70	0.03
283.15	1.403	0.001	333.02	78.76	0.04
283.16	1.399	−0.004	337.99	108.8	0.0
288.13	2.242	−0.020	337.99	108.8	0.0
288.14	2.246	−0.018	340.47	127.0	−0.2

[a] $\Delta p = p - p_{\mathrm{calc}}$, where p_{calc} is calculated from the Clarke and Glew equation with parameters given in Table 9.

Table 7. Experimental Data on Vapor Pressures of 3-PyCOOCH$_3$[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
	Crystalline			Liquid	
273.23	0.651	0.001	298.14	18.19	0.03
273.23	0.658	0.008	298.15	18.19	0.02
278.20	1.228	−0.002	303.13	27.15	−0.06
278.20	1.214	−0.016	303.13	27.12	−0.09
283.18	2.269	−0.004	305.12	31.86	0.03
283.19	2.282	0.006	305.13	31.88	0.03
283.19	2.271	−0.005	307.11	37.12	−0.01
288.16	4.060	−0.048	307.11	37.09	−0.04
288.16	4.076	−0.032	309.10	43.10	−0.10
293.16	7.318	0.036	309.10	43.06	−0.14
293.16	7.304	0.022	311.07	50.20	0.13
298.14	12.70	0.08	311.08	50.06	−0.05
298.16	12.69	0.05	313.07	58.17	0.15
303.14	21.60	0.11	313.08	58.17	0.10
303.14	21.59	0.10	315.06	67.22	0.19
308.10	35.86	0.09	315.07	67.04	−0.04
308.11	35.87	0.06	317.04	77.07	−0.13
310.60	45.66	−0.28	317.05	77.15	−0.11
310.61	45.95	−0.04	318.08	83.17	0.10
310.61	45.57	−0.42	318.11	83.30	0.05
			319.09	88.86	−0.04
			319.09	88.86	−0.29
			321.08	102.0	−0.3
			321.08	103.0	0.7
			323.09	117.7	0.5
			323.09	117.7	0.5
			324.06	124.7	−0.4
			324.06	124.6	−0.5

[a] $\Delta p = p - p_{\mathrm{calc}}$, where p_{calc} is calculated from the Clarke and Glew equation with parameters given in Table 9.

Table 8. Experimental Data on Vapor Pressures of 4-PyCOOCH$_3$[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
	Liquid			Liquid	
273.26	2.588	−0.019	298.13	24.27	−0.04
273.26	2.588	−0.019	298.14	24.28	−0.05
275.74	3.349	0.016	300.63	29.60	−0.05
275.74	3.323	−0.010	300.63	29.61	−0.04
278.22	4.243	0.006	303.12	35.95	−0.04
278.23	4.253	0.012	303.13	35.97	−0.05
280.71	5.373	0.010	305.62	43.47	−0.07
280.71	5.383	0.020	305.63	43.48	−0.10
283.19	6.753	0.006	308.09	52.19	−0.16
283.19	6.753	0.006	308.09	52.19	−0.16
285.66	8.443	0.004	310.59	62.66	−0.18
285.66	8.443	0.004	310.60	62.70	−0.19
288.16	10.54	0.01	313.07	74.95	−0.09
288.16	10.54	0.01	313.07	74.90	−0.14
290.65	13.08	0.01	315.54	89.24	0.01
290.65	13.08	0.01	315.56	89.34	−0.01
293.15	16.15	0.00	318.03	106.2	0.3
293.16	16.17	0.00	318.03	106.2	0.3
295.65	19.90	0.02	320.52	125.6	0.4
295.65	19.90	0.02	320.52	125.6	0.4

[a] $\Delta p = p - p_{\mathrm{calc}}$, where p_{calc} is calculated from the Clarke and Glew equation with parameters given in Table 9.

Table 9. Sublimation and Vaporization Results at $T = 298.15$ K and $p^\circ = 10^5$ Pa

compound	phase	$\Delta_{\mathrm{cd}}^{\mathrm{g}} G_{\mathrm{m}}^0$ J·mol^{-1}	$\Delta_{\mathrm{cd}}^{\mathrm{g}} H_{\mathrm{m}}^0$ kJ·mol^{-1}	$\Delta_{\mathrm{cd}}^{\mathrm{g}} C_{p,\mathrm{m}}^0$ J·K^{-1}·mol^{-1}
2-PyCOOCH$_3$	crystalline	23989 ± 7	81.79 ± 0.14	− 41[a]
2-PyCOOCH$_3$	liquid	24274 ± 3	64.06 ± 0.04	−86 ± 3
3-PyCOOCH$_3$	crystalline	22253 ± 5	80.11 ± 0.13	−41 ± 16
3-PyCOOCH$_3$	liquid	21351 ± 4	61.2 ± 0.21	−107 ± 15
4-PyCOOCH$_3$	crystalline		75.1 ± 0.3[b]	− 41[a]
4-PyCOOCH$_3$	liquid	20626 ± 5	59.37 ± 0.02	−112 ± 3

[a] $\Delta_{\mathrm{cd}}^{\mathrm{g}} C_{p,\mathrm{m}}^0$ estimated according to the value derived for 3-PyCOOCH$_3$ from eq 2 fitting. [b] Estimated from the above value of the enthalpy of vaporization and from the value of the enthalpy of fusion presented in Table 5.

Table 10. Derived Standard ($p^\circ = 0.1$ MPa) Molar Enthalpies of Formation, at $T = 298.15$ K[a]

compound	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^\circ$(cr, l)	$\Delta_{\mathrm{cr,lg}} H_{\mathrm{m}}^\circ$	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^\circ$(g)
2-PyCOOCH$_3$ (l)	−272.9 ± 1.8	64.06 ± 0.04	−208.8 ± 1.8
3-PyCOOCH$_3$ (cr)	−294.2 ± 2.0	80.11 ± 0.13	−214.1 ± 2.0
4-PyCOOCH$_3$ (l)	−278.3 ± 1.8	59.37 ± 0.02	−218.9 ± 1.8

[a] Values in kJ·mol^{-1}.

reference pressure (the gaseous phase is supposed to have characteristics of ideal gas at the pressure p^0), $\Delta_{\mathrm{cd}}^{\mathrm{g}} H_{\mathrm{m}}^0$ is the difference in molar enthalpy between the gaseous and the condensed phase, and $\Delta_{\mathrm{cd}}^{\mathrm{g}} C_{p,\mathrm{m}}^0$ is the difference between the heat capacities of the perfect gas and of the condensed phase. The parameters of the Clarke and Glew equation are presented in Table 9. From the vapor pressure equations the temperature and the pressure of the triple points of the ortho and meta isomers were derived. These values are presented in Table 5 together with the values of the enthalpies of fusion derived from the values of enthalpies of vaporization and of sublimation adjusted for the temperature of fusion using the heat capacity values presented in Table 9. The so derived values for the enthalpies of fusion are in excellent agreement with the values obtained by DSC attesting the reliability of the enthalpies of vaporization and of sublimation derived from the vapor pressure measurements. So these values were selected instead of those obtained from Calvet microcalorimetry for the enthalpy of vaporization of the ortho and para isomers, which are respectively (3 and 6) kJ·mol^{-1} higher than the values derived from vapor pressure measurements. The standard molar enthalpies of formation, in both the condensed and gaseous phases, and the selected values of the enthalpies of sublimation or vaporization for the three compounds are summarized in Table 10.

The enthalpy of sublimation at the temperature of fusion of the para isomer was estimated from the enthalpy of fusion obtained from DSC measurements and from the value of the enthalpy of vaporization adjusted to the temperature of fusion, using the liquid heat capacity value presented in Table 9. The enthalpy of sublimation at the temperature 298.15 K, presented

Table 11. Comparison of Values of Enthalpy of Formation, in the Gaseous State, at T = 298.15 K, Measured in This Work with Literature Values

compound	$\Delta_f H_m^\circ$(g)/kJ·mol^{-1}	X increment/kJ·mol^{-1}
Py	140.4 ± 0.7[34]	
2-PyCOOH	−243.0 ± 2.6[3]	−383.4 ± 2.7
3-PyCOOH	−221.5 ± 1.5[18]	−361.9 ± 1.7
4-PyCOOH	−234.8 ± 4.7[3]	−375.2 ± 4.8
2-PyCOCH$_3$	−41.3 ± 2.9[14]	−181.7 ± 3.0
3-PyCOCH$_3$	−35.2 ± 2.8[14]	−175.6 ± 2.9
4-PyCOCH$_3$	−36.2 ± 2.0[14]	−176.6 ± 2.1
2-PyCOOCH$_3$	−208.8 ± 1.8[a]	−349.2 ± 1.9
3-PyCOOCH$_3$	−214.1 ± 2.0[a]	−354.5 ± 2.1
4-PyCOOCH$_3$	−218.9 ± 1.8[a]	−359.3 ± 1.9
Bz	82.6 ± 0.7[34]	
BzCOOH	−294.1 ± 2.2[34]	−376.7 ± 2.3
BzCOCH$_3$	−86.7 ± 1.7[34]	−169.3 ± 1.8
BzCOOCH$_3$	−276.1 ± 4.0[35]	−358.7 ± 4.1

[a] This work.

Table 12. Enthalpic Increments for the Methylation of the Pyridine Carboxylic Acid Isomers and of Benzoic Acid

compound	$\Delta_f H_m^\circ$(g)/kJ·mol^{-1}	-CH$_3$ increment/ kJ·mol^{-1}
2-PyCOOCH$_3$/2-PyCOOH	−(208.8 ± 1.8)[a]/−(243.0 ± 2.6)[3]	34.2 ± 3.2
3-PyCOOCH$_3$/3-PyCOOH	−(214.1 ± 2.0)[a]/−(221.5 ± 1.5)[18]	7.4 ± 2.5
4-PyCOOCH$_3$/4-PyCOOH	−(218.9 ± 1.8)[a]/−(234.8 ± 4.7)[3]	15.9 ± 5.0
BzCOOCH$_3$/BzCOOH	−(276.1 ± 4.0)[35]/−(294.1 ± 2.2)[34]	18.0 ± 4.6

[a] This work.

in this table, was then calculated using the estimated crystalline heat capacity for this compound.

Conclusion

The results for the enthalpies of formation reported in the present work for the methylpyridine carboxylate isomers are listed in Table 11 together with the values available in literature for the pyridine carboxylic acid and acetylpyridine isomers as well as the values for benzoic acid, acetylbenzene, and methylbenzoate. This table also includes the enthalpic increments for the substitution of the functional groups X = −COOH, −COCH$_3$, and −COOCH$_3$ on the pyridine (Py) and benzene (Bz) molecules. There is evidence of a similar trend and magnitude on the relative variations of the gaseous standard molar enthalpies of formation of pyridine derivatives isomers comparatively with the correspondent benzene derivatives.

The energetic contributions of the functional group −COOCH$_3$, as meta or para substituent on the pyridine ring, compared with the effects observed for identical substitutions of −COOH and −COCH$_3$, show a parallel tendency for the different isomers; however, the effect of the −COOCH$_3$ substitution in ortho position reveals a relative small destabilization of the isomer that is probably due to the steric hindrance of a bulky group located at a carbon adjacent to the heteroatom on the pyridine ring. Indeed, the extended π electron delocalization between the aromatic ring and the group −COOCH$_3$, may be unfavorably affected by the interaction of the lone pair of electrons on the nitrogen.

From our work, it was also possible to calculate the enthalpic increments for the methylation of the pyridine carboxylic acid isomers, which are summarized in Table 12, along with the enthalpic increments for the methylation of benzoic acid. Recently, Roux et al.[35] reported an enthalpic increment of (18.0 ± 4.6) kJ·mol^{-1} for the methylation of benzoic acid, which is in good agreement with the increment for the dimethylation of pyridine-2,6-dicarboxylic acid.[12] The present results point to a similar increment for the methylation of 4-pyridine carboxylic acid and to a higher increment for the methylation of 2-pyridine carboxylic acid. This should reflect the effect of the intramolecular hydrogen bond in 2-pyridine carboxylic acid described by Shahawy et al.[36] on the basis of theoretical SCF−CI calculations.

Literature Cited

(1) Ribeiro da Silva, M. A. V.; Matos, M. A. R. Recent work on the thermochemistry of some nitrogen heterocycles. *Pure Appl. Chem.* **1997**, *69*, 2295−2305.

(2) Ribeiro da Silva, M. A. V. Thermochemistry of substituted pyridines and analogous heterocycles: the enthalpic increments for a group additivity scheme. *Pure Appl. Chem.* **1999**, *71*, 1257−1265.

(3) Ribeiro da Silva, M. D. M. C.; Matos, M. A. R.; Vaz, M. C.; Santos, L. M. B. F.; Pilcher, G.; Acree, W. E., Jr.; Powell, J. R. Enthalpies of combustion of the pyridine N-oxide derivatives: 4-methyl-, 3-cyano-, 4-cyano-, 3-hydroxy-, 2-carboxy-, 4-carboxy-, and 3-methyl-4-nitro, and of the pyridine derivatives: 2-carboxy-, and 4-carboxy-. The dissociation enthalpies of the N−O bonds. *J. Chem. Thermodyn.* **1998**, *30*, 869−878.

(4) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Rio, C. M. A. Standard molar enthalpy of formation of 2,4,6-trimethylpyridine. *J. Chem. Thermodyn.* **1997**, *29*, 901−906.

(5) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, M. L. P. F. Standard molar enthalpies of formation of some chloropyridines. *J. Chem. Thermodyn.* **1997**, *29*, 1535−1543.

(6) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Rio, C. M. A.; Morais, V. M. F. Thermochemical and theoretical studies of 4-methylbiphenyl, 4,4′-dimethylbiphenyl, 4,4′-dimethyl-2,2′-bipyridine. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3061−3065.

(7) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Rio, C. A.; Morais, V. M. F.; Wang, J.; Nichols, G.; Chickos, J. S. A Thermochemical and theoretical study of the phenylpyridine isomers. *J. Phys. Chem. A* **2000**, *104*, 1774−1778.

(8) Ribeiro da Silva, M. D. M. C.; Gonçalves, J. M.; Acree, W. E., Jr. Standard molar enthalpy of sublimation of crystalline 3-pyridinecarboxylic acid. *J. Chem. Thermodyn.* **2000**, *32*, 1071−1073.

(9) Ribeiro da Silva, M. D. M. C.; Gonçalves, J. M.; Ferreira, S. C. C.; da Silva, L. C. M.; Sottomayor, M. J.; Pilcher, G.; Acree, W. E., Jr.; Roy, L. E. Experimental thermochemical study of the enthalpies of formation and sublimation of isonicotinamide, picolinamide, nicotinamide, isonicotinamide N-oxide, and nicotinamide N-oxide. The dissociation enthalpies of the N−O bonds. *J. Chem. Thermodyn.* **2001**, *33*, 1263−1275.

(10) Morais, V. M. F.; Miranda, M. S.; Matos, M. A. R. Thermochemical study of the ethylpyridine and ethylpyrazine isomers. *Org. Biomol. Chem.* **2003**, *1*, 4329−4334.

(11) Gomes, J. R. B.; Amaral, L. M. P. F.; Ribeiro da Silva, M. A. V. Gas-phase thermochemistry of chloropyridines. *Chem. Phys. Lett.* **2005**, *406*, 154−160.

(12) Matos, M. A. R.; Morais, V. M. F.; Ribeiro da Silva, M. D. M. C.; Marques, M. C. F.; Sousa, E. A.; Castiñeiras, J. P.; Santos, C. P.; Acree, W. E., Jr. Thermochemical and theoretical studies of dimethylpyridine-2,6-dicarboxylate and pyridine-2,3-, pyridine-2,5-, and pyridine-2,6-dicarboxylic acids. *J. Chem. Eng. Data* **2005**, *50*, 1184−1191.

(13) Morais, V. M. F.; Miranda, M. S.; Matos, M. A. R. Experimental and computational thermochemistry of the dihydroxypyridine isomers. *J. Chem. Thermodyn.* **2006**, *38*, 450−454.

(14) Freitas, V. L. S.; Oliveira, L. I. P.; Ribeiro da Silva, M. D. M. C. Standard molar enthalpies of formation of the acetylpyridine isomers. *J. Chem. Thermodyn.* (in press).

(15) Trujillo, J. I.; Gopalan, A. S. Facile esterification of sulfonic acids and carboxylic acids with triethylorthoacetate. *Tetrahedron Lett.* **1993**, *34*, 7355−7358.

(16) *Catalogue Handbook of Fine Chemicals and Laboratory Equipment*; The Sigma-Aldrich Chemical Co.: Gillingham, U.K., 2005−2006.

(17) Gundry, H. A.; Harrop, D.; Head, A. J.; Lewis, G. B. Thermodynamic properties of organic oxygen compounds. 21. Enthalpies of combustion of benzoic acid, pentan-1-ol, and hexadecane-1-ol. *J. Chem. Thermodyn.* **1969**, *1*, 321−332.

(18) Bickerton, J.; Pilcher, G.; Al-Takhin, G. Enthalpies of combustion of the three aminopyridines and the three cyanopyridines. *J. Chem. Thermodyn.* **1984**, *16*, 373−378.

(19) Ribeiro da Silva, M. D. M. C.; Santos, L. M. N. B. F.; Silva, A. L. R.; Fernandes, O.; Acree, W. E., Jr. Energetics of 6-methoxyquinoline and 6-methoxyquinoline N-oxide: the dissociation enthalpy of the (N−O) bond. *J. Chem. Thermodyn.* **2003**, *35*, 1093−1100.

(20) Skinner, H. A.; Snelson, A. The heats of combustion of the four isomeric butyl alcohols. *Trans. Faraday Soc.* **1960**, *56*, 1776−1783.

(21) Coops, J.; Jessup, R. S.; Van Nes, K. Calibration of calorimeters for reactions in a bomb at constant volume. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, pp 27−58.

(22) Wagman, D. D.; Evans, W. H.; Parker V. B.; Schumm R. H.; Halow I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. The NBS tables of chemical thermodynamic properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(23) Washburn, E. W. Standard states for bomb calorimetry. *J. Res. Natl. Bur. Stand.* (*U.S.*). **1933**, *10*, 525−558.

(24) Hubbard, W. N.; Scott, D. W.; Waddington, G. Standard states and corrections for combustions in a bomb at constant volume. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, pp 75 − 127.

(25) Adedeji, F. A.; Lalage, D.; Brown, S.; Connor, J. A.; Leung, M. L.; Paz Andrade, I. M.; Skinner, H. A. Thermochemistry of arene chromium tricarbonyls and the strenghts of arene-chromium bonds. *J. Organomet. Chem.* **1975**, *97*, 221−228.

(26) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. Thermochemical study of 2-, 4-, 6-, and 8-methylquinoline. *J. Chem. Thermodyn.* **1995**, *27*, 565−574.

(27) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(28) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of sublimation of organic and organometallic compounds, 1910−2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537−698.

(29) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of vaporization of organic and organometallic compounds, 1880−2002. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519−878.

(30) Loss, R. D. Atomic weights of the elements 2001 (IUPAC Technical Report). *Pure Appl. Chem.* **2003**, *75*, 1107−1122.

(31) Monte, M. J. S.; Santos, L. M. N. B. F.; Fulem, M.; Fonseca, J. M. S.; Sousa, C. A. D. New static apparatus and vapor pressure of reference materials: naphthalene, benzoic acid, benzophenone, and ferrocene. *J. Chem. Eng. Data* **2006**, *51*, 757−766.

(32) Rossini, F. D. Assignment of uncertainties to thermochemical data. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, pp 297−319.

(33) CODATA recommended key values for thermodynamics. *J. Chem. Thermodyn.* **1978**, *10*, 903−906.

(34) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*, Vol 1; Thermodynamics Research Center: College Station, TX, 1994.

(35) Roux, M. V.; Temprado, M.; Dávalos, J. Z.; Jiménez, P.; Hosmane, R. S.; Liebman, J. F. Enthalpy of formation of methyl benzoate: calorimetry and consequences. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3611−3613.

(36) Shahawy, A. S.; Seleim, M. M.; Saleh, M. S. J. Hydrogen bonds affecting the structure of picolinic and anthranilic acids. *Proc. Pak. Acad. Sci.* **1988**, *25*, 81−89.

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