Thermochemistry of substituted pyridines and analogous heterocycles: the enthalpic increments for a group additivity scheme*

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Abstract: Values available in the literature for the standard ($p° = 0.1\,\text{MPa}$) molar enthalpies of formation in the gaseous phases, at temperature 298.15 K, for substituted pyridines, such as methylpyridines, hydroxypyridines, aminopyridines, cyanopyridines, chloropyridines and bromopyridines are reviewed, discussed and interpreted in terms of contributions from atoms, bonds and group of atoms as well as their interactions within the molecules. The enthalpic increments for each group contribution are calculated and suggested as parameters for a Group Additivity Scheme for the estimation of standard molar enthalpies of formation, in the gaseous state, of substituted pyridines. The validity of this approach is verified for different substituted pyridines. The scheme is tested with experimental values available for the standard molar enthalpies of formation of substituted quinolines.

INTRODUCTION

The demands of the ever increasing development of Science and Technology requires a reliable and as vast as possible databank on Thermodynamic and Kinetic values, such as standard molar enthalpies of formation, bond dissociation enthalpies, energies of activation, etc. Such data are important to the understanding of chemical problems, such as energetics of the chemical bonds, structural properties and reactivity and on even more applied fields like chemical industry, biochemistry, medical and life sciences, environmental chemistry, military matters, etc.

There is, however, an enormous difference between the size of the experimental thermochemical databanks and the number of known molecules, and this gap increases everyday, since it is impossible to measure the thermochemical properties for all the known compounds and for the new ones prepared everyday. At present, the situation is such that thermochemical data on some classes of compounds, such as hydrocarbons and other aliphatic compounds, are well known and of excellent quality but on other classes, like aromatic and heterocycle compounds, those data are scarce or even totally lacking. Therefore it is important to have reliable methods for estimating the enthalpies of formation of different classes of compounds. At the moment, there are several well-established schemes for the estimation of these properties for gaseous aliphatic and alicyclic compounds [1] but for the gaseous aromatic compounds those empirical bond-energy schemes do not apply because they do not account for the effect of perturbation on the π-electron systems. Based on the experimental data available for the standard molar enthalpies of formation, in the gaseous state, of substituted benzenes, Cox [2] suggested a scheme based on a constant increment in $\Delta_f H°_m(g)$ on substitution of a particular group, independent of the position of the substituent, which was refined by applying correction terms concerning the relative positions on polysubstituted compounds. For heterocycle compounds, the situation is even more difficult and problematic, since not only a consistent predicting scheme for these compounds does not exist, but also because well-established experimental values for the key compounds are still scarce.

In order to contribute to the improvement of this situation, the experimental values available in the literature for the standard ($p° = 0.1$ MPa) molar enthalpies of formation in the gaseous phase, at temperature 298.15 K, for substituted pyridines, are reviewed, the increments of the different substituents, in the different positions, on the $\Delta_f H°_m$(g) of the molecules are calculated, and a group additvity scheme for the estimation of the standard molar enthalpies of formation of substituted pyridines is suggested, and checked with the different substituted pyridines for which the standard molar enthalpies of formation in the gaseous state have been experimentally determined. This scheme is tested with the experimental values of $\Delta_f H°_m$(g) for substituted quinolines.

THERMOCHEMICAL PARAMETERS FOR SUBSTITUTED PYRIDINES

The available values of the standard molar enthalpies of formation of substituted pyridines, on the condensed phase, were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry (rotating bomb calorimetry was used in the case of the halogen pyridines), with the amount of substance used in each experiment determined from the total amount of carbon dioxide produced [3,4].

The standard molar enthalpies of vaporisation or sublimation necessary for the calculation of the standard molar enthalpies of formation in the gaseous phase were obtained by different experimental methods, as described in the original references.

Monosubstituted pyridines

Literature values for the standard molar enthalpies of formation, in the gaseous state, for methyl (Me-py), hydroxy (OH-py), amino (NH$_2$-py), cyano (CN-py), chloro (Cl-py) and bromo (Br-py) monosubstituted pyridines are summarized in Table 1.

Table 1 Standard ($p° = 0.1$ MPa) molar quantities, at $T = 298.15$ K (values in kJ/mol)

Compound	X-py	$\Delta_f H°_m$(g)	X-increment	
Pyridine	py	140.4 ± 0.7 [5]	–	–
2-Methylpyridine	2-Mepy	99.2 ± 0.7 [5]	o-Me	−41.2 ± 1.0
3-Methylpyridine	3-Mepy	106.5 ± 0.6 [5]	m-Me	−33.9 ± 0.9
4-Methylpyridine	4-Mepy	104.0 ± 0.9 [5]	p-Me	−36.4 ± 1.1
2-Hydroxypyridine	2-OHpy	−79.7 ± 1.3 [6]	o-0H	−220.1 ± 1.5
3-Hydroxypyridine	3-OHpy	−43.7 ± 1.5 [6]	m-OH	−184.1 ± 1.7
4-Hydroxypyridine	4-OHpy	−30.5 ± 5.3 [7]	p-OH	−170.7 ± 5.3
2-Aminopyridine	2-NH$_2$py	118.1 ± 1.1 [8]	o-NH$_2$	−22.3 ± 2.2
3-Aminopyridine	3-NH$_2$py	144.2 ± 1.6 [8]	m-NH$_2$	3.8 ± 1.8
4-Aminopyridine	4-NH$_2$py	129.9 ± 1.4 [8]	p-NH$_2$	−10.5 ± 1.6
2-Cyanopyridine	2-CNpy	280.7 ± 1.5 [8]	o-CN	140.3 ± 1.7
3-Cyanopyridine	3-CNpy	277.9 ± 2.0 [8]	m-CN	137.5 ± 1.2
4-Cyanopyridine	4-CNpy	283.5 ± 1.0 [8]	p-CN	143.1 ± 1.2
2-Chloropyridine	2-Clpy	104.5 ± 1.8 [9]	o-Cl	−35.9 ± 1.9
3-Chloropyridine	3-Clpy	107.6 ± 1.7 [9]	m-Cl	−32.8 ± 1.8
2-Bromopyridine	2-Brpy	160.4 ± 2.1 [10]	o-Br	20.0 ± 2.2
3-Bromopyridine	3-Brpy	167.1 ± 2.1 [10]	m-Br	26.7 ± 2.2

The enthalpy increments for the introduction of a group, or an halogen atom, into the pyridine ring, are calculated as the difference between the standard molar enthalpies of formation, in the gaseous phase, of the substituted pyridine and of the pyridine itself

$$X - \text{increment} = \Delta_f H°_m(X - py, g) - \Delta_f H°_m(py, g)$$

and are registered in Table 1.

Di- and trimethylpyridines

The literature values of the standard molar enthalpies of formation, at $T = 298.15$ K, in the gaseous state, of the six isomers of dimethylpyridine, as well as of the 2,4,6-trimethylpyridine are shown in Table 2.

Table 2 Experimental and estimated standard ($p° = 0.1$ MPa) molar enthalpies of formation of di- and trimethylpyridines, in the gaseous state, at $T = 298.15$ K

| Me$_n$py | $\Delta_f H°_m$(g) (kJ/mol) | | | Δ (kJ/mol) |
	experimental	calculated		
2,3-Me$_2$py	67.1 ± 1.3^{5}	py + o-Me + m-Me =	65.3 ± 1.5	-1.8 ± 2.3
2,4-Me$_2$py	63.6 ± 0.8^{5}	py + o-Me + p-Me =	62.8 ± 1.6	-0.8 ± 1.8
2,5-Me$_2$py	66.5 ± 1.0^{5}	py + o-Me + m-Me =	65.3 ± 1.5	-1.2 ± 1.8
2,6-Me$_2$py	58.1 ± 1.5^{5}	py + o-Me + o-Me =	58.0 ± 1.6	-0.1 ± 2.2
3,4-Me$_2$py	68.8 ± 1.0^{5}	py + m-Me + p-Me =	70.1 ± 1.6	1.3 ± 1.9
3,5-Me$_2$py	72.0 ± 0.9^{5}	py + m-Me + m-Me =	72.6 ± 1.5	-0.6 ± 1.7
2,4,6-Me$_3$py	19.3 ± 2.4^{11}	py + 2(o-Me) + p-Me =	21.6 ± 1.9	2.3 ± 3.1

Considering the enthalpic increments for the monomethylation of pyridine registered in Table 1, $-(41.2 \pm 1.0)$, $-(33.9 \pm 0.9)$ and $-(36.4 \pm 1.1)$ in the positions *ortho*, *meta* and *para*, respectively, and the standard molar enthalpy of formation of the gaseous pyridine (140.4 ± 0.7) kJ/rnol [5], one can estimate the standard molar enthalpies of formation of the polymethylated pyridines. These values are collected in Table 2 with the differences Δ between the experimental and estimated values. From these values, one can conclude that the estimated values reproduce, within the experimental associated uncertainties, the experimental values of $\Delta_f H°_m$(g) in all cases, even when both methyl groups enter in the *ortho* position, one relative to the other, and so it seems that in the pyridine there is transferability of the group enthalpic contributions for methyl substitutions.

Figure 1 shows the experimental and the estimated (values between brackets) enthalpic increments on the standard molar enthalpy of formation for the mono-, di- and trimethylation of gaseous pyridine, showing the good agreement between each experimental/estimated pair of values.

From the available values for the standard molar enthalpies of formation of pyrazine and methylsubstituted pyrazines, which are summarized in Table 3, it was concluded in a previous paper [12] that the increment for the tetramethylation of pyrazine, $\Delta_f H°_m = -(141.3 \pm 4.7)$ kJ/mol, is twice that verified for the dimethylation, $-(70.0 \pm 5.2)$, as shown in Table 3.

However, the standard molar enthalpy of formation of trimethylpyrazine shows that $\Delta_f H°_m$, the enthalpy increment for trimethylation of pyrazine, $-(121.7 \pm 3.1)$ kJ/mol is not simply equal to 0.75 of the tetramethylation enthalpy increment, $-(105.9 \pm 7.8)$ kJ/mol, meaning that successive methylations of pyrazine are not the sum of individual increments alone. This experimental fact is confirmed by the theoretical estimates of the electronic energy, using Density Function Theory (DFT) [12], which correlate well with the experimental values for the standard molar enthalpies of formation of the three methylated pyrazines studied.

It can therefore be concluded that whilst in pyridine there is transferability of group enthalpy contributions for methyl substitutions, this is not the case for pyrazine. This may be due to the presence of a second nitrogen atom in the pyrazine ring.

Hydroxy-2-methylpyridines

The experimental values of the standard molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K, for each of the four isomeric hydroxy-2-methylpyridines are available in the literature [6], thus making it possible to test the validity of the transferability of the hydroxy group enthalpy
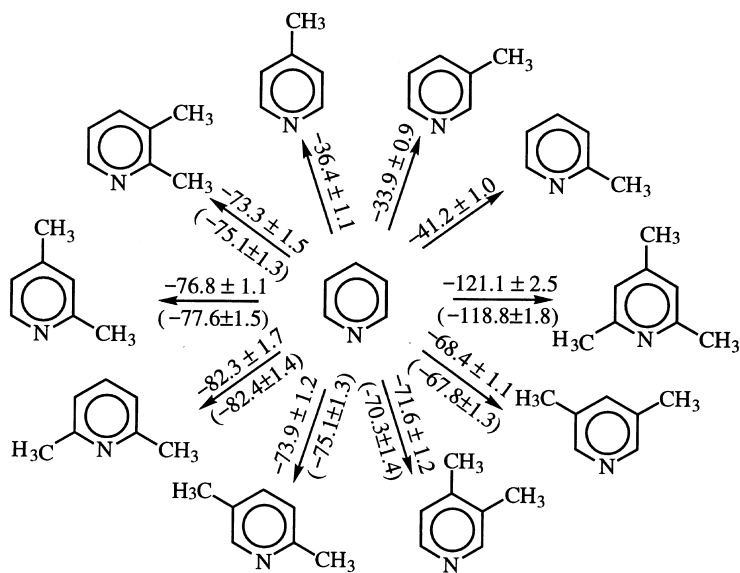
Fig. 1 Enthalpic increments for the di- and trimethylation of pyridine. The experimental increments are indicated on the upper side of the arrows, and the estimated ones are between brackets, on the lower of the arrows.

Table 3 Standard ($p° = 0. 1$ MPa) molar enthalpies of formation of pyrazines, in the gaseous state, at $T = 298.15$ K, and the enthalpy increments $\Delta_r H°_m$ due to successive methyl substitutions

Compound	$\Delta_f H°_m$(g) (kJ/mol)	$\Delta_f H°_m$ (kJ/mol)*	
		experimental	estimated
Pyrazine	196.0 ± 1.5 [13]	–	–
2,3-Dimethylpyrazine	126.0 ± 5.0 [12]	-70.0 ± 5.2	–
Trimethylpyrazine	74.3 ± 2.7 [12]	-121.7 ± 3.1	-105.9 ± 7.8
Tetramethylpyrazine	54.7 ± 4.5 [12]	-141.3 ± 4.7	-140.0 ± 7.4

* $\Delta_r H°_m = \Delta_f H°_m$(Me$_n$pyrazine, g) $- \Delta_f H°_m$(Pyrazine, g), $n =$ number of methyl substituents on the molecule.

contributions in the pyridine ring. Table 4 summarizes the experimental values of the standard molar enthalpies of formation, of the four hydroxy-2-methylpyridines, the estimated ones using the enthalpic increments registered in Table 1 for the -OH substitutions in the *ortho*, *meta* and *para* positions, and also the differences Δ between the experimental and the estimated values.

Table 4 Experimental and estimated standard ($p° = 0.1$ MPa) molar enthalpies of formation of hydroxy-2-methylpyridines, in the gaseous state, at $T = 298.15$ K

OH-2-Mepy	$\Delta_f H°_m$(g) (kJ/mol)			Δ (kJ/mol)
	experimental	calculated		
2-Mepy	99.2 ± 0.7[5]	–	–	–
3-OH-2-Mepy	-84.4 ± 1.5[6]	2-Mepy $+ m$-OH =	-84.9 ± 1.8	-0.5 ± 2.4
4-OH-2-Mepy	-71.7 ± 1.5[6]	2-Mepy $+ p$-OH =	-71.5 ± 5.3	0.2 ± 5.5
5-OH-2-Mepy	-69.8 ± 2.4[6]	2-Mepy $+ m$-OH =	-84.9 ± 1.8	-15.1 ± 3.0
6-OH-2-Mepy	-120.3 ± 2.3[6]	2-Mepy $+ o$-OH =	-120.9 ± 1.7	-0.6 ± 2.9

The Δ values show that, except for 5-hydroxy-2-methylpyridine, the estimated values reproduce the experimental values of $\Delta_f H°_m(g)$, giving support to the transferability of group enthalpic contributions for hydroxy substitutions into the pyridine ring. There is no obvious reason for the discrepancy between the experimental and calculated values of $\Delta_f H°_m(g)$ of 5-hydroxy-2-methylpyridine, and this discrepancy strongly suggests the experimental remeasurement of its standard molar enthalpies of formation and sublimation.

Figure 2 shows the experimental and estimated (values between brackets) enthalpic increments on the standard molar enthalpy of formation for the hydroxylation of gaseous 2-methylpyridine, showing the good agreement between them, except for the case of 5-hydroxy-2-methylpyridine.
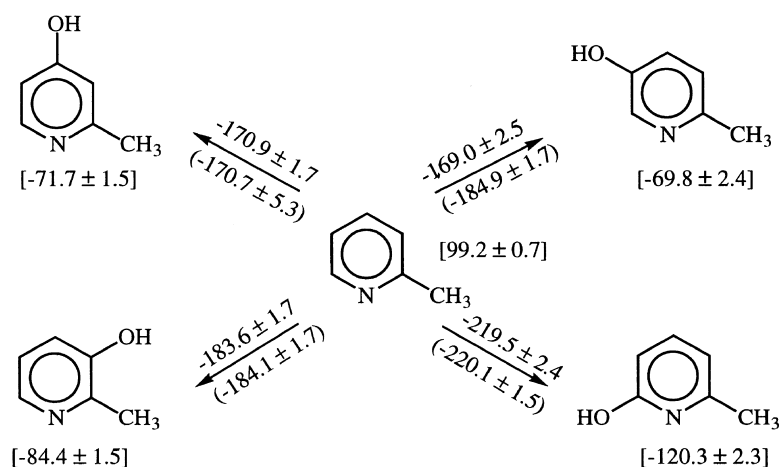

Fig. 2 Enthalpic increments for the hydroxylation of gaseous 2-methylpyridine. The experimental increments are indicated on the upper side of the arrows, and the estimated ones are between brackets on the lower side of the arrows. The $\Delta_f H°_m(g)$ of each compound is indicated between square brackets.

Dihalogenopyridines

The available literature values of the standard molar enthalpies of formation at $T = 298.15$ K, in the gaseous state, of dichloropyridines and dibromopyridines are shown in Table 5. The estimated values of the standard molar enthalpies of formation of these compounds, using the enthalpic increments registered in Table 1 for the -Cl and -Br substitutions on the *ortho* and *meta* positions, and also the differences Δ between the experimental and the estimated values of $\Delta_f H°_m(g)$ are also registered in Table 5.

Table 5 Experimental and estimated standard ($p° = 0.1$ MPa) molar enthalpies of formation of dichloropyridines and dibromopyridines, in the gaseous state, at $T = 298.15$ K

X$_2$py	$\Delta_f H°_m(g)$ (kJ/mol)			Δ (kJ/mol)
	experimental	calculated		
2,3-Cl$_2$py	89.5 ± 3.4 [9]	py + *o*-Cl + *m*-Cl + 4 =	75.7 ± 2.7	-13.8 ± 4.3
2,5-Cl$_2$py	71.5 ± 2.2 [9]	py + *o*-Cl + *m*-Cl =	71.7 ± 2.7	0.2 ± 3.5
2,6-Cl$_2$py	71.4 ± 1.9 [9]	py + *o*-Cl + *o*-Cl =	68.6 ± 2.8	-2.8 ± 3.4
3,5-Cl$_2$py	82.2 ± 2.1 [9]	py + M-Cl + M-Cl =	74.8 ± 2.6	-7.4 ± 3.3
2,5-Br$_2$py	190.2 ± 2.5 [10]	py + *o*-Br + *m*-Br =	187.1 ± 3.2	-3.1 ± 4.1
2,6-Br$_2$py	182.9 ± 3.3 [10]	py + *o*-Brl + *o*-Br =	180.4 ± 3.2	-2.5 ± 4.6

The enthalpy increments for the entrance of a chlorine atom in the *ortho* and *meta* positions of pyridine are $-(35.9 \pm 1.9)$ kJ/mol and $-(32.8 \pm 1.5)$ kJ/mol, respectively, as shown in Table 1. For the bromination of pyridine on the *ortho* and *meta* positions, these increments are, respectively (20.0 ± 2.2) kJ/mol and (26.7 ± 2.2) kJ/mol as registered in Table 1. Using these enthalpic increments and an enthalpy increment term of $+4$ kJ/mol for each *ortho*-pair of halogen substituents, as suggested by Cox [2] on his scheme for benzene derivatives, the standard molar enthalpies of formation for the different dichloropyridines and dibromopyridines were estimated and figure in Table 5, together with the differences Δ between the experimental and the estimated values. The good agreement between the experimental and estimated values, with the exception of 2,3-dichloropyridine, for which there is no explanation at the moment, suggests that the transferability of halogen enthalpic contributions can be used to estimate $\Delta_f H^\circ_m(g)$ of halogenopyridines. The discrepancy observed for 2,3-dichloropyridine suggests a remeasurement of this compound.

The experimental and estimated (values between brackets) enthalpic increments on the standard molar enthalpies of formation for the halogenation of gaseous pyridine are shown in Fig. 3 for the bromination and in Fig. 4 for the chlorination.
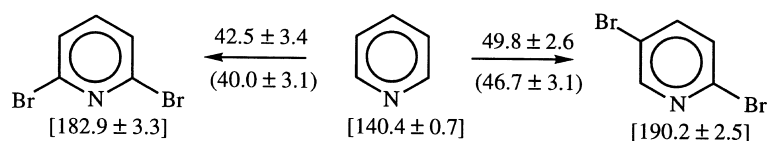

Fig. 3 Enthalpic increments for the bromination of gaseous pyridine. The experimental increments are indicated on the upper side of the arrows, and the estimated ones are, between brackets, on the lower side of the arrows. The $\Delta_f H^\circ_m(g)$ of each compound is indicated between square brackets.
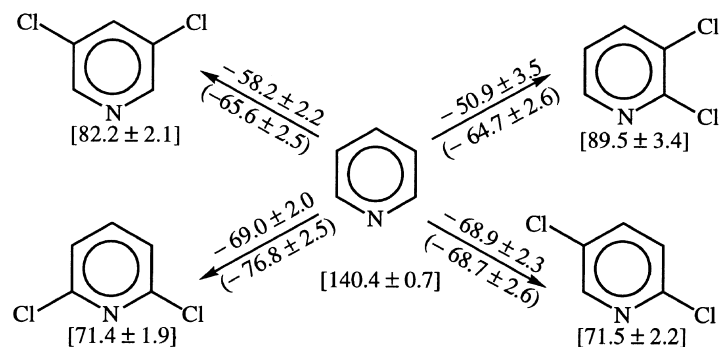

Fig. 4 Enthalpic increments for the chlorination of gaseous pyridine. The experimental increments are indicated on the upper side of the arrows, and the estimated ones are, between brackets, on the lower side of the arrows. The $\Delta_f H^\circ_m(g)$ of each compound is indicated between square brackets.

QUINOLINE DERIVATIVES

The validity of this Group Additivity Scheme for the estimation of standard molar enthalpies of formation, in the gaseous state, may be tested on the quinoline derivatives, since quinoline has one pyridine ring on its structure. Figure 5 shows the molecular structure of quinoline and the way of numbering the different carbon atoms in order to identify the different derivatives from quinoline.

In order to check the validity of the Scheme, only derivatives with substituents in the pyridinic ring of the quinoline molecule are considered. Table 6 registers the available standard molar enthalpies of formation, in the gaseous state, at $T = 298.15$ K, of the quinoline derivatives with substituents in the pyridinic ring.

For the hydroxymethylquinolines, with both the hydroxy and the methyl groups in the pyridine ring,
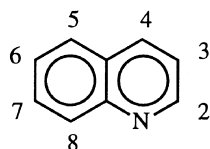
Fig. 5 Molecular structure of quinoline

Table 6 Experimental and estimated standard ($p° = 0.1$ MPa) molar enthalpies of formation of quinoline derivatives, in the gaseous state, at $T = 298.15$ K

| | $\Delta_f H°_m$(g) (kJ/mol) | | |
Compound	experimental	estimated	Δ (kJ/mol)
Quinoline	200.54 ± 0.94[14]	–	–
8-Hydroxyquinoline	6.5 ± 1.7[10]	–	–
2-Methylquinoline	159.1 ± 3.1[7]	159.3 ± 1.4	0.2 ± 3.4
4-Methylquinoline	162.1 ± 3.2[7]	164.1 ± 1.4	2.0 ± 3.5
2-Hydroxyquinoline	-25.5 ± 2.4[9]	-19.6 ± 1.8	5.9 ± 3.0
4-Hydroxyquinoline	20.8 ± 2.3[9]	29.8 ± 5.4	9.0 ± 5.9
2-Hydroxy-4-methylquinoline	-61.0 ± 2.3[9]	-61.9 ± 2.6*	-0.9 ± 4.1
4-Hydroxy-2-methylquinoline	-23.3 ± 2.9[9]	-20.4 ± 2.5†	2.9 ± 3.8
8-Hydroxy-2-methylquinoline	-39.4 ± 2.2[10]	-34.7 ± 2.0	4.7 ± 3.0
2-Aminoquinoline	208.4 ± 2.2[11]	204.3 ± 2.0	-4.1 ± 3.0
2-Cyanoquinoline	340.9 ± 2.7[12]	340.8 ± 1.9	-0.1 ± 3.3
3-Cyanoquinoline	336.5 ± 2.2[12]	338.0 ± 2.3	1.5 ± 3.2

*Value estimated considering the methylation of 2-hydroxyquinoline.
†Value estimated considering the methylation of 4-hydroxyquinoline.

there are three different ways of estimating their standard molar enthalpies of formation, depending on the starting compound considered to apply the enthalpic increments of the group contribuitions. So, for 2-hydroxy-4-methylquinoline, if one starts from quinoline, adding the increment for the *o*-OH group, $-(220.1 \pm 1.5)$ kJ/mol, and for the *p*-Me group, $-(36.4 \pm 1.1)$ kJ/mol, we estimate $\Delta_f H°_m$(g) $-(56.0 \pm 2.0)$ kJ/mol; if we start from 4-methylquinoline and add the increment for *o*-OH group, the estimation gives $\Delta_f H°_m$(g) $= -(58.0 \pm 3.5)$ kJ/mol; finally, starting from 2-hydroxyquinoline and considering the increment for the *para*-methylation, $-(36.4 \pm 1.1)$ kJ/mol, we estimate $\Delta_f H°_m$(g) $-(61.9 \pm 2.6)$ kJ/mol. This last approach yields the estimated value which is closer to the experimental one. In a similar way, the standard molar enthalpy of formation of 4-hydroxy-2-methylquinoline can also be estimated by three different routes: starting from the quinoline and adding the enthalpic increments for the *p*-OH group $-(170.7 \pm 5.3)$ kJ/mol and for the *o*-Me group $-(41.2 \pm 1.0)$ kJ/mol, the estimation gives $\Delta_f H°_m$(g) $= -(11.4 \pm 5.5)$ kJ/mol; if one starts from 2-methylquinoline and add the increment for the *p*-OH group, $-(170.7 \pm 5.3)$ kJ/mol the estimated value is $\Delta_f H°_m$(g) $= -(11.6 \pm 5.3)$ kJ/mol; finally, starting from the 4-hydroxyquinoline and considering the group increment for the *o*-methylation, $-(41.2 \pm 1.0)$ kJ/mol, the estimated value is $\Delta_f H°_m$(g) $= -(20.4 \pm 2.5)$ kJ/mol, again, the estimation closer to the experimental value.

It is important to notice that the estimated values which are closer to the experimental ones, are those estimated by the route in which the starting compounds are the hydroxyquinolines, to which the group contributions for methylation are added. This suggests that the application of the enthalpic increments of the –OH groups on the pyridinic ring of quinoline must be done with special care, being more accurate to start from the hydroxyquinolines and adding the enthalpic contributions of the other groups, instead of considering the starting contribution of each group having the pyridine molecule as the starting one. This procedure is supported by the results shown in Table 6, which shows that the estimated standard molar

enthalpies of formation of 2-and 4-hydroxyquinolines have somewhat large deviations, respectively, (5.9 ± 3.0) kJ/mol and (9.0 ± 5.9) kJ/mol from the experimental values. On the other hand, if we calculate the –OH enthalpic increments in the hydroxyquinolines with respect to the quinoline, we obtain for the *ortho*-hydroxy substitution an increment of $-(225.7 \pm 2.6)$ kJ/mol and for the *para*-hydroxy substitution an increment of $-(179.7 \pm 2.5)$ kJ/mol. Using these increments to estimate the standard molar enthalpies of formation of the gaseous 2-hydroxy-4-methylquinoline and 4-hydroxy-2-methylquinoline, by adding the appropriate increments of the hydroxy and methyl groups to the quinoline, we estimate $\Delta_f H^\circ_m$ (2-OH-4-MeQ, g) $-(61.6 \pm 3.0)$ kJ/mol and $\Delta_f H^\circ_m$ (4-OH-2-MeQ, g) $-(20.4\ 2.9)$ kJ/mol, values which are in excellent agreement with the experimental ones registered in Table 6.

This good agreement between experimental and estimated values gives confidence to the experimental results obtained for the hydroxyquinolines and hydroxymethylquinolines and indicates that for the estimation of the standard molar enthalpies of formation of substituted hydroxyquinolines it is more accurate to start from the experimental values of the hydroxyquinolines instead of the quinoline itself.

CONCLUSIONS

The difference Δ between the estimated and the experimental enthalpies of formation of substituted pyridines (Tables 2, 4 and 5) and of quinoline derivatives with substituents in the pyridine ring (Table 6) show that the additivity scheme for substituted pyridines works quite well, except for two of the compounds of which the experimental standard molar enthalpies of formation are known: 5-hydroxy-2-methylpyridine and 2,3-dichloropyridine. At the moment there is no explanation for this behaviour and so a careful remeasurement of the thermochemical parameters of these two compounds is strongly desirable.

As stated before, in the case of substituted hydroxyquinolines, the hydroxy enthalpy increments calculated from the hydroxyquinolines themselves yield better estimations than if the hydroxy enthalpy increments from pyridine are used.

Table 7 shows the enthalpic increments in the standard molar enthalpies of formation for substituted pyridines, which we suggest as a Group Additivity Scheme for substituted pyridines.

Table 7 Enthalpic increments in the standard molar enthalpies of formation of substituted pyridines

| -X | $\partial [\Delta_f H^\circ_m(g)]$ (kJ/mol) | | |
	o-X	*m*-X	*p*-X
-CH$_3$	-41.2 ± 1.0	-33.9 ± 0.9	-36.4 ± 1.1
-OH	-220.1 ± 1.5	-184.1 ± 1.7	-170.7 ± 5.3
-NH$_2$	-22.3 ± 2.2	3.8 ± 1.8	-10.5 ± 1.6
-CN	140.3 ± 1.7	137.5 ± 2.1	143.1 ± 1.2
-Cl	-35.9 ± 1.9	-32.8 ± 1.8	–
-Br	20.0 ± 2.2	26.7 ± 2.2	–

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