

## THERMOCHEMICAL STUDY OF THREE DIMETHYLPYRAZINE DERIVATIVES

Maria D. M. C. Ribeiro da Silva<sup>1\*</sup>, Joana I. T. A. Cabral<sup>1</sup>, Chelsea Givens<sup>2</sup>,  
Stephanie Keown<sup>2</sup> and W. E. Acree Jr.<sup>2</sup>

<sup>1</sup>Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre 687 4169-007 Porto, Portugal

<sup>2</sup>Department of Chemistry, University of North Texas, Denton, TX 76203-5070, USA

The standard ( $p^0=0.1$  MPa) molar enthalpies of formation, in the gaseous phase, at  $T=298.15$  K, for 2,5-dimethylpyrazine (2,5-DMePz) and for the two dimethylpyrazine- $N,N'$ -dioxide derivatives, 2,3-dimethylpyrazine-1,4-dioxide (2,3-DMePzDO) and 2,5-dimethylpyrazine-1,4-dioxide (2,5-DMePzDO), were derived from the measurements of standard massic energies of combustion, using a static bomb calorimeter, and from the standard molar enthalpies of vaporization or sublimation, measured by Calvet microcalorimetry.

The mean values for the molar dissociation enthalpy of the nitrogen–oxygen bonds,  $\langle DH_m^0 \rangle(N-O)$ , were derived for both  $N,N'$ -dioxide compounds. These values are discussed in terms of the molecular structure of the two  $N,N'$ -dioxide derivatives and compared with  $\langle DH_m^0 \rangle(N-O)$  values previously obtained for other  $N$ -oxide derivatives.

**Keywords:** 2,5-dimethylpyrazine, 2,3-dimethylpyrazine-1,4-dioxide, 2,5-dimethylpyrazine-1,4-dioxide, dimethylsubstituted pyrazine  $N,N'$ -dioxides, enthalpy of formation, mean  $N-O$  bond dissociation enthalpy, sublimation enthalpy, vaporization enthalpy

### Introduction

The thermochemical study of the heterocyclic nitrogen molecules with  $N-O$  bonds has received a special interest from researchers of our Thermochemistry Group [1]. Particular attention has been devoted to derivatives from phenazine  $N,N'$ -dioxide [2], quinoxaline  $N,N'$ -dioxide [3–9] and pyrazine  $N,N'$ -dioxide [3, 10], in order to clarify the relationship between the energetics, structure and reactivity of those heterocyclic nitrogen compounds containing a ring with two nitrogen atoms in positions 1,4. The experimental results reported in the present work mean a new contribution to enlarge the knowledge about the properties and chemical behaviour of the pyrazine  $N,N'$ -dioxide derivatives.

The present work reports the standard ( $p^0=0.1$  MPa) molar enthalpies of formation, in the gaseous phase, at  $T=298.15$  K, of 2,5-dimethylpyrazine (2,5-DMePz) and two dimethylpyrazines- $N,N'$ -dioxide derivatives, 2,3-dimethylpyrazine-1,4-dioxide (2,3-DMePzDO) and 2,5-dimethylpyrazine-1,4-dioxide (2,5-DMePzDO), derived from the measurements of standard massic energies of combustion, using a static bomb calorimeter, and from the standard molar enthalpies of vaporization or sublimation, measured by Calvet microcalorimetry.

The mean values for the molar dissociation enthalpies of the nitrogen–oxygen bonds,  $\langle DH_m^0 \rangle(N-O)$ , were derived for both  $N,N'$ -dioxide derivatives.

### Experimental

#### Compounds and purity control

2,3-Dimethylpyrazine-1,4-dioxide (2,3-DMePzDO) and 2,5-dimethylpyrazine-1,4-dioxide (2,5-DMePzDO) were prepared by hydrogen peroxide oxidation of 2,3-dimethylpyrazine and 2,5-dimethylpyrazine according to the published synthetic procedure of Klein and Berkowitz [11]. The crude product was removed from the sodium hydroxide neutralized reaction mixture, by chloroform extraction. The resulting chloroform extractant was concentrated under reduced pressure to about one-third of its original volume and then diluted with an equal quantity of cold 2,2,4-trimethylpentane. The solid product that was formed was collected by vacuum filtration and further purified by vacuum sublimation. Elemental analyses were in excellent agreement with calculated values: mass fractions for 2,3-DMePzDO,  $C_6H_8N_2O_2$ : found: C, 0.5132; H, 0.0570; N, 0.2008; calculated: C, 0.5142; H, 0.0575; N, 0.1999 and for 2,5-DMePzDO,  $C_6H_8N_2O_2$ : found: C, 0.5143;

\* Author for correspondence: mdsilva@fc.up.pt

H, 0.0565; N, 0.2010; calculated: C, 0.5142; H, 0.0575; N, 0.1999.

2,5-Dimethylpyrazine (2,5-DMePz), supplied by Aldrich Chemical with initial purity of 0.98 mass fraction was purified by fraction distillation under reduced pressure. The purity was checked by GLC and by the carbon dioxide recovery from the combustion measurements.

The average ratios of the mass of carbon dioxide recovered after combustion, to that calculated from the mass of sample, were: for

- 2,5-DMePz (1.00003±0.00010),
- 2,3-DMePzDO (0.99926±0.00012),
- 2,5-DMePzDO (0.99950±0.00005)

where the uncertainties are the standard deviations of the means. The density of 2,5-DMePz was assumed to be  $\rho=0.99 \text{ g cm}^{-3}$  [12] and the density of the crystalline samples was estimated from the mass and the dimensions of the pellet: 2,3-DMePzDO,  $\rho=1.29 \text{ g cm}^{-3}$  and 2,5-DMePzDO,  $\rho=1.32 \text{ g cm}^{-3}$ .

#### Combustion calorimetry

The standard massic energies of combustion of the compounds studied experimentally, i.e. 2,5-DMePz, in the liquid-state, and 2,3-DMePzDO and 2,5-DMePzDO, both in the solid phase, were measured by static bomb combustion calorimetry, using two different isoperibol static bomb calorimeters: Calorimeter 1 for 2,5-DMePz, and Calorimeter 2 for the other two compounds.

In the experiments performed with Calorimeter 1, a twin valve bomb, model 1105 (Parr Instrument, Illinois, USA) of internal volume  $0.340 \text{ cm}^3$  was used. A detailed description of the apparatus and the technique can be found in the literature [13, 14]. The bomb used with Calorimeter 2 has an internal volume of  $0.290 \text{ cm}^3$  and the description of this combustion calorimeter can also be found in [15–17]. Both calorimeters were calibrated by combustion of thermochemical standard benzoic acid, sample NBS 39j, with  $\Delta_c u = -26434 \pm 3 \text{ J g}^{-1}$  [18], under experimental conditions, and found to be  $\varepsilon_{\text{cal}} = 15905.70 \pm 0.74 \text{ J K}^{-1}$ , for Calorimeter 1, and  $\varepsilon_{\text{cal}} = 15546.3 \pm 1.3 \text{ J K}^{-1}$ , for Calorimeter 2. The calibrations followed the procedure previously described [19], and the results corrected to give the energy equivalents,  $\varepsilon_{\text{cal}}$ , corresponding to the average mass of water added to the calorimeters of 3119.6 and 2900.0 g, respectively, for Calorimeter 1 and Calorimeter 2. The uncertainties quoted are the standard deviations of the mean, of at least 6 experiments for Calorimeter 1 and 8 for Calorimeter 2.

The liquid samples of 2,5-DMePz were burnt enclosed in previously weighed sealed polyester bags

made of Melinex with 0.025 mm of thickness, with a massic energy of combustion of  $\Delta_c u^0 = -22902 \pm 5 \text{ J g}^{-1}$  [20] corrected for the mass fraction of water  $w=0.0032$  [20].

The solid compounds were pressed into pellet form. As 2,3-DMePzDO is hygroscopic, the pellets were also burnt enclosed in sealed Melinex bags, to prevent the absorption of moisture during the experiment. For the experiments with 2,5-DMePzDO, *n*-hexadecane (Aldrich Gold Label, mass fraction >0.999), stored under nitrogen, was used as combustion auxiliary. The massic energy of combustion of *n*-hexadecane, measured in our Laboratory, was found to be  $\Delta_c u^0 = -47160.8 \pm 4.1 \text{ J g}^{-1}$ .

All substances were burnt in an oxygen atmosphere with  $1.00 \text{ cm}^3$  of water added to the bomb, at an initial pressure of 3.04 MPa, after purging the bomb twice with oxygen to remove the air. The calorimetric temperatures were measured at time intervals of 10 s, and at least 100 readings were taken for each the fore, the main and the after periods. The ignition was made at  $T=298.150 \pm 0.001 \text{ K}$ , by the discharge of a  $1400 \mu\text{F}$  capacitor through the platinum ignition wire. A cotton thread fuse with empirical formula of  $\text{CH}_{1.686}\text{O}_{0.843}$  was used, with a massic energy of combustion of  $-\Delta_c u^0 = 16250 \text{ J g}^{-1}$  [19]. At the end of each combustion experiment, the amount of compound burnt in that experiment was determined from the total mass of  $\text{CO}_2$  produced taking into account that formed from cotton-thread fuse and from Melinex or *n*-hexadecane, in the cases they were used. The amount of  $\text{HNO}_3$  formed was determined by titration of the aqueous solution resulting from washing the inside of the bomb.

#### Microcalorimetry Calvet

The standard molar enthalpy of vaporization of 2,5-DMePz, and the standard molar enthalpies of sublimation of 2,3-DMePzDO and 2,5-DMePzDO were determined with a Calvet High Temperature Microcalorimeter (Setaram, HT 1000D) using for the liquid compound a similar technique [21] to that described for the sublimation of solids by Skinner *et al.* [22]. The apparatus and technique have been described [23].

Samples, of about 5 mg of the liquid and 3 mg of the solid compounds, contained in thin glass capillary tubes sealed at one end, were dropped from room temperature into the hot zone of the calorimeter, held at a predefined convenient temperature,  $T$ , for the study of the vaporization or sublimation of the compounds, and then removed from the hot zone by vacuum vaporization or sublimation, depending on the compound. The thermal corrections for the glass capillaries were made

by dropping tubes of nearly equal mass simultaneously into the experimental and the reference cell.

In this work, the calorimeter was held at  $T=329$  K for 2,5-DMePz and at  $T=442$  K for 2,3-DMePzDO and 2,5-DMePzDO. At  $T=329$  K, the calibration of the calorimeter was made with *n*-undecane, 99+, supplied by Aldrich Chemical Co., using the value of  $\Delta_1^s H_m^0 = 56.580 \pm 0.566$  kJ mol<sup>-1</sup> for the standard molar enthalpy of vaporization of the *n*-undecane at  $T=298.15$  K [24]. From 6 independent experiments, the value of the calibration constant for that temperature was  $k_{\text{cal}} (T=329 \text{ K}) = 1.0104 \pm 0.0012$ , with the uncertainty as the standard deviation of the mean. At  $T=442$  K, the value of the calibration constant was found to be  $k_{\text{cal}} (T=442 \text{ K}) = 1.0037 \pm 0.0033$ , determined by sublimation of naphthalene, using the value of  $\Delta_{\text{cr}}^s H_m^0$  (naphthalene, cr) =  $72.60 \pm 0.60$  kJ mol<sup>-1</sup> [24], at  $T=298.15$  K. The values of the enthalpies of vaporization/sublimation of *n*-undecane and naphthalene, at the temperature  $T$  of the calibration experiments, were calculated from their values at  $T=298.15$  K using literature values of  $\Delta_{298.15\text{K}}^T H_m^0$  (g), from Stull *et al.* [25]. The experimental procedure for the calibration experiments was the same as the one used on the experiments with the studied compounds.

## Results and discussion

Results for a typical combustion experiment of each compound are given in Table 1, where  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water added to the calorimeter from 3119.6 g (Calorimeter 1) or 2900.0 g (Calorimeter 2), with the internal energy for the isothermal bomb process,  $\Delta U_{\text{I.B.P.}}$ , calculated according to the equation:  $\Delta U_{\text{I.B.P.}} = -\{\varepsilon_{\text{cal}} + \Delta m_{\text{H}_2\text{O}} c_p(\text{H}_2\text{O}(l) + \varepsilon_f)\Delta T_{\text{ad}} + \Delta U_{\text{ignition}}$ .  $\Delta U$  (fuse) is the energy of combustion of the cotton-thread fuse;  $\Delta U$  (Melinex) and  $\Delta U$  (hexadecane) are, respectively, the energy of combustion of the Melinex and *n*-hexadecane used in the experiments. The corrections for nitric acid formation,  $\Delta U(\text{HNO}_3)$ , were based on  $-59.7$  kJ mol<sup>-1</sup>, for the molar energy of formation of 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub>(aq), from N<sub>2</sub>(g), O<sub>2</sub>(g) and H<sub>2</sub>O(l) [26] and  $\Delta U(\text{ign})$  is the electrical energy supplied for ignition. For each compound, an estimated pressure coefficient of massic energy,  $(\partial u/\partial p)_T$ , at  $T=298.15$  K, was assumed to be  $-0.2$  J g<sup>-1</sup> MPa<sup>-1</sup>, a typical value for most organic compounds [27]. The correction to the standard state,  $\Delta U_{\Sigma}$ , and the massic energy of combustion,  $\Delta_c u^0$ , were calculated by the procedure of Hubbard *et al.* [28].

**Table 1** Results of a typical combustion experiment, at  $T=298.15$  K

Experiment	2,5-DMePz	2,3-DMePzDO	2,5-DMePzDO
$m(\text{CO}_2, \text{total})/\text{g}$	2.18629	0.82086	1.24500
$m(\text{cpd})/\text{g}$	0.83955	0.38813	0.58475
$m(\text{Melinex})/\text{g}$	0.05734	0.03739	–
$m(\text{fuse})/\text{g}$	0.00309	0.00242	0.00393
$m(\text{hexadecane})/\text{g}$	–	–	0.04400
$\Delta T_{\text{ad}}/\text{K}$	1.83267	0.67832	1.07451
$\varepsilon_f/\text{J K}^{-1}$	16.59	15.33	15.68
$\Delta m(\text{H}_2\text{O})/\text{g}$	+0.1	+2.2	+0.1
$-\Delta U(\text{I.B.P.})^a/\text{J}$	29180.23	10561.01	16720.75
$\Delta U(\text{Melinex})/\text{J}$	1313.12	856.22	–
$\Delta U(\text{fuse})/\text{J}$	50.18	39.30	63.82
$\Delta U(\text{hexadecane})/\text{J}$	–	–	2074.43
$\Delta U(\text{HNO}_3)/\text{J}$	73.67	27.52	45.97
$\Delta U(\text{ign})/\text{J}$	0.84	1.00	1.20
$\Delta U_{\Sigma}/\text{J}$	18.29	7.43	10.91
$-\Delta_c u^0/\text{J g}^{-1}$	33023.61	24812.66	24840.74

$m(\text{CO}_2, \text{total})$  – total mass of carbon dioxide recovered in the combustion;  $m(\text{cpd})$  – mass of compound burnt in each experiment;  $m(\text{Melinex})$  – mass of Melinex used to enclose the compounds;  $m(\text{fuse})$  – mass of the cotton thread fuse;  $m(\text{hexadecane})$  – mass of hexadecane;  $\Delta T_{\text{ad}}$  – adiabatic temperature rise;  $\varepsilon_f$  – energy equivalent of the calorimeter including the contents of the bomb in the final state;  $\Delta m(\text{H}_2\text{O})$  – deviation of the mass of water added to the calorimeter from 3119.6 g (Calorimeter 1) or 2900.0 g (Calorimeter 2);  $\Delta U(\text{IBP})$  – energy change for isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{Melinex})$  – energy of combustion of the Melinex used in each experiment;  $\Delta U(\text{fuse})$  – energy of combustion of the fuse (cotton);  $\Delta U(\text{hexadecane})$  – energy of combustion of hexadecane;  $\Delta U(\text{HNO}_3)$  – energy correction for the nitric acid formation;  $\Delta U(\text{ign})$  – electrical energy supplied for ignition,  $\Delta U_{\Sigma}$  – standard state correction;  $\Delta_c u^0$  – massic energy of combustion of the compound. <sup>a</sup> $\Delta U(\text{I.B.P.})$  already includes  $\Delta U(\text{ign})$

**Table 2** Individual values of the massic energy of combustion,  $\Delta_c u^0$ , for the compounds, at  $T=298.15$  K

2,5-DMePz	2,3-DMePzDO	2,5-DMePzDO
	$-\Delta_c u^0/\text{J g}^{-1}$	
33023.61	24812.66	24825.83
33024.94	24868.96	24853.83
32982.57	24841.34	24860.98
32982.09	24882.22	24840.74
33002.75	24835.41	24841.59
32994.92	24843.99	24818.51
	24824.75	
	$-\langle\Delta_c u^0\rangle/\text{J g}^{-1}$	
33001.8±7.6	24844.2±9.1	24840.2±6.6

The relative atomic masses used were those recommended by the IUPAC Commission in 2005 [29]. For all compounds studied, the individual values of  $\Delta_c u^0$ , together with the mean and its standard deviation, are given in Table 2.

Table 3 lists, for each compound, the derived standard molar values for the energy ( $\Delta_c U_m^0$ ) and enthalpy ( $\Delta_c H_m^0$ ) of combustion and the standard molar enthalpy of formation,  $\Delta_f H_m^0$ , in the condensed phase.

The uncertainties of the standard molar energies and enthalpies of combustion are twice the final overall standard deviation of the mean, and include the uncertainties in calibration [30, 31] as well as the respective uncertainties of the auxiliary compounds used.

The values of the standard molar enthalpies of formation in the condensed phase,  $\Delta_f H_m^0$  (l or cr), were derived from  $\Delta_c H_m^0$ , using the values, at  $T=298.15$  K, of the standard molar enthalpies of formation of liquid water and gaseous carbon dioxide, respectively,

$\Delta_f H_m^0(\text{H}_2\text{O}, \text{l}) = -285.830 \pm 0.042$  kJ mol<sup>-1</sup> [32] and  $\Delta_f H_m^0(\text{CO}_2, \text{g}) = -393.51 \pm 0.13$  kJ mol<sup>-1</sup> [32].

Results of the microcalorimetric determinations of the enthalpy of vaporization of 2,5-DMePz or the enthalpies of sublimation of 2,3-DMePzDO and 2,5-DMePzDO, are given in the Table 4. The values of the enthalpies of vaporization or sublimation, at the experimental temperature  $T$ , correspond to the mean values of 5 experiments for 2,5-DMePz and 6 for the other two compounds, with uncertainties given by their standard deviations. The observed molar enthalpies of vaporization or sublimation,  $\Delta_{\text{l or cr}, T}^{\text{g}} H_m^0$ , were corrected to  $T=298.15$  K using  $\Delta_{298.15 \text{ K}}^{\text{T}} H_m^0(\text{g})$  estimated by a group scheme based on the values of Stull *et al.* [25]. The schemes applied for these corrections are:

2,5-dimethylpyrazine=2(2-methylpyridine)–benzene

2,3-dimethylpyrazine  $N,N'$ -dioxide=  
2(2-methylpyridine)–benzene+2(N–O)

2,5-dimethylpyrazine  $N,N'$ -dioxide=  
2(2-methylpyridine)–benzene+2(N–O)

which gives, at  $T=329$  K,  $\Delta_{298.15 \text{ K}}^{329.0 \text{ K}} H_m^0(2,5\text{-DMePz}) = 3.90$  kJ mol<sup>-1</sup> and at  $T=442$  K,  $\Delta_{298.15 \text{ K}}^{442.2 \text{ K}} H_m^0(2,3\text{-DMePzDO}) = 25.12$  kJ mol<sup>-1</sup> and  $\Delta_{298.15 \text{ K}}^{442.0 \text{ K}} H_m^0(2,5\text{-DMePzDO}) = 25.06$  kJ mol<sup>-1</sup>. The uncertainties associated to the standard enthalpies of vaporization or sublimation, at  $T=298.15$  K, are twice the standard deviation of the mean and include the uncertainty associated with the calibration procedure.

The combination of the values of the standard molar enthalpies of formation in the condensed state, together with the enthalpies of vaporization or sublimation, yield the standard molar enthalpies of formation of the studied compounds in the gaseous state, which are registered in Table 5.

**Table 3** Derived standard ( $p^0=0.1$  MPa) molar energies of combustion,  $\Delta_c U_m^0$ , standard molar enthalpies of combustion,  $\Delta_c H_m^0$ , and standard molar enthalpies of formation for the compounds in the condensed phase,  $\Delta_f H_m^0$  (l or cr), at  $T=298.15$  K

Compound	$-\Delta_c U_m^0/\text{kJ mol}^{-1}$	$-\Delta_c H_m^0/\text{kJ mol}^{-1}$	$\Delta_f H_m^0(\text{l or cr})/\text{kJ mol}^{-1}$
2,5-DMePz(l)	3568.9±1.8	3571.4±1.8	67.0±2.0
2,3-DMePzDO(cr)	3481.7±3.1	3481.7±3.1	-22.7±3.2
2,5-DMePzDO(cr)	3481.1±2.0	3481.1±2.0	-23.3±2.2

**Table 4** Microcalorimetric standard ( $p^0=0.1$  MPa) molar enthalpies of vaporization or sublimation, at  $T=298.15$  K


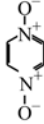

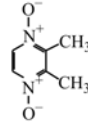
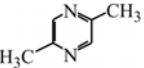
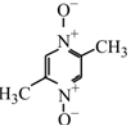
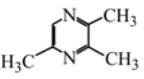
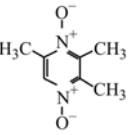
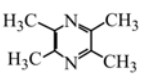
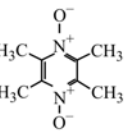
Compound	No. of experiments	$T/\text{K}$	$\Delta_{\text{l or cr}, T}^{\text{g}} H_m^0/\text{kJ mol}^{-1}$	$\Delta_{298 \text{ K}}^{\text{T}} H_m^0(\text{g})/\text{kJ mol}^{-1}$	$\Delta_{\text{l or cr}}^{\text{g}} H_m^0(T=298.15 \text{ K})/\text{kJ mol}^{-1}$
2,5-DMePz(l)	5	329.0	52.81±0.21	3.90	48.9±1.1
2,3-DMePzDO(cr)	6	442.2	140.11±0.35	25.12	115.0±2.1
2,5-DMePzDO(cr)	6	442.0	147.00±0.58	25.06	121.9±2.4

## THREE DIMETHYLPYRAZINE DERIVATIVES

**Table 5** Derived standard ( $p^0=0.1$  MPa) molar enthalpies of formation,  $\Delta_f H_m^0$ , and of vaporization or sublimation,  $\Delta_{1\text{ or cr}}^g H_m^0$ , at  $T=298.15$  K

Compound	$\Delta_f H_m^0(\text{l or cr})/\text{kJ mol}^{-1}$	$\Delta_{1\text{ or cr}}^g H_m^0/\text{kJ mol}^{-1}$	$\Delta_f H_m^0(\text{g})/\text{kJ mol}^{-1}$
2,5-DMePz(l)	67.0±2.0	48.9±1.1	115.9±2.3
2,3-DMePzDO(cr)	-22.7±3.2	115.0±2.1	92.3±3.8
2,5-DMePzDO(cr)	-23.3±2.2	121.9±2.4	98.6±3.5

**Table 6** Comparison of the mean bond dissociation enthalpies derived in this work with others reported in the literature

	$\Delta_f H_m^0(\text{g})/\text{kJ mol}^{-1}$		$\Delta_f H_m^0(\text{g})/\text{kJ mol}^{-1}$	$\langle DH_m^0 \rangle(\text{N-O})/\text{kJ mol}^{-1}$
 Pz	196.1±1.3 [34]	 PzDO	186.5±1.9 [3]	254.0±1.2 [3]
 2,3-DMePz	126 [33]	 2,3-DMePzDO	92.3±3.8 <sup>a</sup>	266.0±3.8 <sup>a</sup>
 2,5-DMePz	115.9±2.3 <sup>a</sup>	 2,5-DMePzDO	98.6±3.5 <sup>a</sup>	257.8±4.0 <sup>a</sup>
 2,3,5-TrMePz	74.3±2.7 [33]	 2,3,5-TrMePzDO	45.7±3.2 [10]	263.5±3.4 [10]
 2,3,5,6-TeMePz	54.7±4.5 [33]	 2,3,5,6-TeMePzDO	1.0±3.4 [10]	276.0±5.5 [10]

<sup>a</sup>This work

## Conclusions

The mean (N–O) bond dissociation enthalpies,  $\langle DH_m^0 \rangle(\text{N-O})$ , for a polymethylpyrazine  $N,N'$ -dioxide,  $x\text{MePzDO}(\text{g})$ , can be derived as one half of the enthalpy of the gaseous reaction (1).



In order to derive the values of  $\langle DH_m^0 \rangle(\text{N-O})$  for the  $N,N'$ -dioxide compounds studied in this work and registered in Table 6, the following literature values have been used:  $\Delta_f H_m^0(\text{O}, \text{g})=249.18 \pm 0.10$  kJ mol<sup>-1</sup> [32] and  $\Delta_f H_m^0(2,3\text{-DMePz}, \text{g})=126$  kJ mol<sup>-1</sup> [33]. Table 6 resumes also the relevant literature values for other pyrazine dioxides.

Considering a thermodynamic reactivity scale, for an oxygen atom transfer process [1] involving the compounds reported in this work, the results of  $\langle DH_m^0 \rangle(\text{N-O})$  obtained for the two dimethylpyrazine  $N,N'$ -dioxides and the previous data reported in literature for pyrazine  $N,N'$ -dioxide [3], tri- and tetramethylpyrazine  $N,N'$ -dioxides [10] seem to be consistent, pointing to a decrease of the tendency in 2,3-dimethylpyrazine  $N,N'$ -dioxide to promote oxidation comparatively with pyrazine  $N,N'$ -dioxide. This effect seems to be neglected when the electron donating groups CH<sub>3</sub> are in opposite positions 2,5.

Examination of the numerical entries in Table 6 further shows that the placement of two adjacent CH<sub>3</sub> groups onto the pyrazine ring system increases the mean  $DH(\text{N-O})$  bond dissociation enthalpy by approxi-

mately  $12 \text{ kJ mol}^{-1}$ , from  $\langle DH_m^0 \rangle(\text{N-O})=254.0 \pm 1.2 \text{ kJ mol}^{-1}$  for pyrazine *N,N'*-dioxide to  $\langle DH_m^0 \rangle(\text{N-O})=266.0 \pm 3.8 \text{ kJ mol}^{-1}$  for 2,3-dimethylpyrazine *N,N'*-dioxide. To within experimental uncertainty, the addition of the second two adjacent  $\text{CH}_3$  groups to form 2,3,5,6-tetramethylpyrazine *N,N'*-dioxide results in about another  $12 \text{ kJ mol}^{-1}$  increase in the value.

## Acknowledgements

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química, University of Porto. Joana I. T. A. Cabral thanks FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of a Post-Doc research grant (BPD/27140/2006). Chelsea Givens and Stephanie Keown thanks the National Science Foundation for support received under NSF-REU grant (CHE-0243795).

## References

- W. E. Acree Jr., G. Pilcher and M. D. M. C. Ribeiro da Silva, *J. Phys. Chem. Ref. Data*, **34** (2005) 553.
- J. R. B. Gomes, E. A. Sousa, J. M. Gonçalves, M. J. S. Monte, P. Gomes, S. Pandey, W. E. Acree Jr. and M. D. M. C. Ribeiro da Silva, *J. Phys. Chem. B*, **109** (2005) 16188.
- W. E. Acree Jr., J. R. Powell, S. A. Tucker, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, J. M. Gonçalves, L. M. N. B. F. Santos, V. M. F. Morais and G. Pilcher, *J. Org. Chem.*, **62** (1997) 3722.
- M. D. M. C. Ribeiro da Silva, J. R. B. Gomes, J. M. Gonçalves, E. A. Sousa, S. Pandey and W. E. Acree Jr., *J. Org. Chem.*, **69** (2004) 2785.
- M. D. M. C. Ribeiro da Silva, J. R. B. Gomes, J. M. Gonçalves, E. A. Sousa, S. Pandey and W. E. Acree Jr., *Org. Biomol. Chem.*, **2** (2004) 2507.
- J. R. B. Gomes, M. D. M. C. Ribeiro da Silva and M. A. V. Ribeiro da Silva, *Chem. Phys. Lett.*, **429** (2006) 18.
- J. R. B. Gomes, E. A. Sousa, P. Gomes, N. Vale, J. M. Gonçalves, S. Pandey, W. E. Acree Jr. and M. D. M. C. Ribeiro da Silva, *J. Phys. Chem. B*, **111** (2007) 2075.
- J. R. B. Gomes, E. A. Sousa, J. M. Gonçalves, L. Gales, A. M. Damas, P. Gomes, S. Pandey, W. E. Acree Jr. and M. D. M. C. Ribeiro da Silva, *J. Phys. Org. Chem.*, **20** (2007) 491.
- J. R. B. Gomes, M. A. A. Vieira, D. M. Stovall, W. E. Acree Jr. and M. D. M. C. Ribeiro da Silva, *Bull. Chem. Soc. Jpn.*, **80** (2007) 1770.
- M. D. M. C. Ribeiro da Silva, M. A. A. Vieira, C. Givens, S. Keown and W. E. Acree Jr., *Thermochim. Acta*, **450** (2006) 67.
- B. Klein and J. Berkowitz, *J. Amer. Chem. Soc.*, **81** (1959) 5160.
- www.sigmaaldrich.com
- M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *Rev. Por. Quím.*, **26** (1984) 163.
- M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *J. Chem. Thermodyn.*, **16** (1984) 1149.
- H. A. Gundry, D. Harrop, A. J. Head and G. B. Lewis, *J. Chem. Thermodyn.*, **1** (1969) 321.
- J. Bickerton, G. Pilcher and G. Al-Takhin, *J. Chem. Thermodyn.*, **16** (1984) 373.
- M. D. M. C. Ribeiro da Silva, L. M. N. B. F. Santos, A. L. R. Silva, Ó. Fernandes and W. E. Acree, *J. Chem. Thermodyn.*, **35** (2003) 1093.
- Certificate of Analysis Standard Reference Material 39j Benzoic Acid Calorimetric Standard. NBS, Washington 1995.
- J. Copps, R. S. Jessup and K. Van Nes, *Experimental Thermochemistry*, F. D. Rossini, Ed., Vol. 1, Interscience, New York 1956, Chapter 3.
- H. A. Skinner and A. Snelson, *Trans. Faraday Soc.*, **56** (1960) 1776.
- M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, *J. Chem. Thermodyn.*, **27** (1995) 565.
- F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, *J. Organomet. Chem.*, **97** (1975) 221.
- L. M. N. B. F. Santos, B. Schröder, O. O. P. Fernandes and M. A. V. Ribeiro da Silva, *Thermochim. Acta*, **415** (2004) 15.
- R. Sabbah, A. Xu-Wu, J. D. Chickos, M. L. Planas Leitão, M. V. Roux and L. A. Torres, *Thermochim. Acta*, **331** (1999) 93.
- R. D. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York 1969.
- D. D. Wagmar; W. H. Evans, V. B. Parker, R. H. Shum, F. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11** Suppl. 2 (1982).
- E. N. Washburn, *J. Res. Natl. Bur. Stand. (U.S.)*, **10** (1933) 525.
- W. N. Hubbard, D. W. Scott and G. Waddington, *Experimental Thermochemistry*, F. D. Rossini, Ed., Vol. 1, Interscience, New York 1956, Chapter 5.
- E. Weise, *Pure Appl. Chem.*, **78** (2006) 2051.
- F. D. Rossini, *Experimental Thermochemistry*, F. D. Rossini, Ed., Vol. 1, Interscience, New York 1956, Chapter 14.
- G. Olofsson, *Combustion Calorimetry*, S. Sunner, M. Månsson, Eds, Pergamon, Oxford 1979, Chapter 6.
- J. D. Cox, D. D. Wagman and V. A. Medvedev, *CODATA Key Values for Thermodynamics*, Hemisphere, New York 1989.
- M. A. V. Ribeiro da Silva, V. M. F. Morais, M. A. R. Matos, C. M. A. Rio and C. M. G. S. Piedade, *Struct. Chem.*, **7** (1996) 329.
- J. Tjebbes, *Acta Chem. Scand.*, **16** (1962) 916.

DOI: 10.1007/s10973-007-8737-9