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GAS PHASE ENTHALPY OF FORMATION OF 3-BROMOQUINOLINE

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The standard (p^0=0.1 MPa) molar enthalpy of formation, $\Delta_f H_m^0(l)$=169.8±2.6 kJ mol^{-1}, of the liquid 3-bromoquinoline was derived from its standard molar energy of combustion, in oxygen, to yield $CO_2(g)$, $N_2(g)$ and $HBr\cdot600H_2O(l)$, at T=298.15 K, measured by rotating bomb combustion calorimetry. The Calvet high temperature vacuum sublimation technique was used to measure the enthalpy of vaporization of the compound, $\Delta_l^g H_m^0$=70.7±2.3 kJ mol^{-1}. These two thermodynamic parameters yielded the standard molar enthalpy of formation, in the gaseous phase, at T=298.15 K, $\Delta_f H_m^0(g)$=240.5±3.5 kJ mol^{-1}.

Keywords: *3-bromoquinoline, Calvet microcalorimetry, combustion calorimetry, rotating bomb calorimetry, standard molar enthalpy of formation, thermochemistry*

Introduction

Quinoline is an aromatic nitrogen compound containing a benzene ring fused to a pyridine ring producing a heterocycle with two aromatic rings. Polymer sciences, metallurgical applications, dyes, rubber chemicals and fungicides, all provide extensive examples for their use but medical field and the pharmaceutical industry are the major driving force in the synthesis and properties of molecules containing these structures. Halogenated quinolines are selective PDE III inhibitors [1] and are effective to treat sexual dysfunctions in males and females, including, but not limited to, erectile dysfunction in males. PDE III is a cyclic nucleotide phosphodiesterase [2, 3] that is an enzyme which is clinically significant because of its role in regulating heart muscle, vascular smooth muscle and platelet aggregation, so PDE III inhibitors have been developed as pharmaceuticals but their use is limited by arrhythmic effects and they can increase mortality in some applications.

As a part of our extensive work on the thermochemistry of nitrogen heterocyclic compounds we have studied several quinolines derivatives in order to see if an estimation scheme, similar to Cox scheme for benzenes [4] can be applied for quinolines. In this paper we report the standard (p^0= 0.1 MPa) molar enthalpy of formation, of the liquid 3-bromoquinoline derived from its standard massic energy of combustion in oxygen, to yield $CO_2(g)$, $N_2(g)$ and $HBr\cdot600H_2O(l)$, at T=298.15 K, measured by rotating bomb combustion calorimetry. The Calvet high temperature vacuum sublimation technique was used to measure the enthalpy of vaporization of this compound. These two thermodynamic parameters yielded the standard molar enthalpy of formation of 3-bromoquinoline, in the gaseous phase, at T=298.15 K.

Experimental

Materials

Compound and purity control

The 3-bromoquinoline was obtained commercially from Aldrich Chemical Co., [CAS 5332-24-1] and was purified by repeated distillation under reduced pressure. The purity of the sample was checked by microanalysis at the Department of Chemistry, University of Aveiro; the mass fractions w of C, H and N were as follows: Found, $10^2\ w(C)=0.520$, $10^2\ w(H)=0.029$ and $10^2\ w(N)=0.067$; calculated for C_9H_6NBr: $10^2\ w(C)=0.517$, $10^2\ w(H)=0.030$ and $10^2\ w(N)=0.067$.

The specific density, used to calculate the true mass from apparent mass in air was $\rho=1.533$ g cm^{-3} [5].

Methods

Combustion calorimetry

The combustion experiments were performed with an isoperibol rotating-bomb calorimeter, developed by Sunner [6] at the University of Lund, Sweden. The apparatus and the technique have been described in

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the literature [7, 8]. The bomb, whose internal volume is 0.258 dm^3, is of stainless steel lined with platinum, with the internal fittings also machined from platinum. In each experiment, the bomb is suspended from the lid of the calorimeter can, to which 5222.5 g of water, previously weighed in a perspex vessel, is added. For each experiment a correction to the energy equivalent was made for the deviation of the mass of water used to the reference mass of 5222.5 g.

Calorimeter temperatures were measured to $\pm 10^{-4}$ K at time intervals of 10 s, using a Hewlett-Packard (HP-2804A) quartz thermometer interfaced to an Olivetti M 250E microcomputer programmed to compute the corrected temperature change. For each experiment, the ignition temperature was chosen so that the final temperature would be close to T= 298.15 K. Fore-period and after-period readings were taken for about 20 min and the main-period was about 25 min. Data acquisition and control of the calorimeter was performed through the use of the LABTERMO programme [9].

The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb. Rotation of the bomb was started when the temperature rise in the main-period reached about 0.63 of its total value and was continued throughout the rest of the experiment. By adopting this procedure, described by Good *et al.* [10], the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket.

The isothermal jacket consists of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in overall dimensions, enclosed by a hollow lid. The jacket and lid were filled with water maintained at a temperature $303.5 \pm \approx 10^{-4}$ K, using a temperature controller (Tronac PTC 41), so that the calorimeter was completely surrounded by a constant-temperature enclose.

Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard BCS-CRM-190p) was used for the calibration of the bomb. Its massic energy of combustion is -26431 ± 3.7 J g^{-1} under certificate conditions. Calibration experiments were carried out in oxygen, at the pressure of 3.04 MPa, with 1.00 cm^3 of water added to the bomb. Two calibration constants were used on the combustion experiments of 3-bromoquinoline since the calorimeter went through some repairs during the period time of these experiments: ε(calor)=25181.1±1.4 J K^{-1}, and ε(calor)= 25180.8±1.6 J K^{-1}, where the uncertainties quoted are the standard deviation of the mean.

The combustion experiments were made in oxygen at p=3.04 MPa, in the presence of 20.00 cm^3 of aqueous As_2O_3 0.09415 and 0.09759 mol dm^{-3} solutions, in order to reduce to hydrobromic acid all the free bromine produced during the combustion. The extent of oxidation of As_2O_3(aq) was determined by titration with standardized iodine solution. For the calculation of the energetic term $\Delta U(As_2O_3)$ corresponding to the energy of oxidation of As_2O_3 to As_2O_5 in aqueous solution, the procedure described by Hu *et al.* [11] as well as the enthalpies of oxidation of As_2O_3(aq) by Br_2 [12] and the thermal effects of mixing As_2O_5(aq) with strong acids [13] were used. Within the precision of the analytical method, no evidence was found for the oxidation of the aqueous solution of As_2O_3 after the bomb had been charged with oxygen at p=3.04 MPa and left up to 5 h at room temperature [14]. The amount of H_2PtBr_4(aq) was determined from the loss of mass from the platinum crucible and its supporting ring.

The liquid 3-bromoquinoline was burnt in sealed polyester bags made of Melinex® using the technique described by Skinner and Snelson [15] who determined the massic energy of combustion of dry Melinex® as $\Delta_c u^0 = -22902 \pm 5$ J g^{-1}; this value was previously confirmed in our laboratory. The mass of Melinex® used in each experiment was corrected for the mass fraction of water (0.0032).

The electrical energy for ignition was determined from the change in potential difference across a 1400 μF condenser discharged through a platinum wire (ϕ=0.05 mm, Goodfellow, mass fraction 0.9999).

For the cotton thread fuse used for the ignition, whose empirical formula is $CH_{1.686}O_{0.843}$, $\Delta_c u^0$= –16240 J g^{-1} [16], a value previously confirmed in our laboratory.

The nitric acid formed was determined using the Devarda's alloy method [17] and corrections were based on –59.7 kJ mol^{-1} for the molar energy of formation in which 0.1 mol dm^{-3} HNO_3(aq) is formed from $O_2(g)$, $N_2(g)$ and $H_2O(l)$ [18]. An estimated value of the pressure coefficient of massic energy, $(\partial u/\partial p)_T = -0.2$ J g^{-1} MPa^{-1} at T=298.15 K, a typical value for most organic compounds [19], was assumed for 3-bromoquinoline. For each compound the standard state corrections, ΔU_Σ, and the heat capacities of the bomb contents, ε_i and ε_f, were calculated by the produce given by Bjellerup [20] using the solubility constants and energies of solution of CO_2 and O_2, as given by Hu *et al.* [11].

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005 [21].

High temperature microcalorimetry

The standard molar enthalpy of vaporization of 3-bromoquinoline was measured using the vacuum sublimation drop-microcalorimetric technique [22, 23].

Table 1 Standard (p^0=0.1 MPa) massic energy of combustion of 3-bromoquinoline, at T=298.15 K

	1	2	3	4	5	6	7	8	9
m(compound)/g	0.88150	0.81783	0.73064	0.83487	0.70949	0.66235	0.68456	0.91582	1.02689
m'(fuse)/g	0.00324	0.00344	0.00305	0.00358	0.00343	0.00300	0.00294	0.00297	0.00281
m''(Melinex®)/g	0.05074	0.05826	0.05978	0.05503	0.05548	0.05439	0.06428	0.06835	0.06000
$(\varepsilon_{cal})_{corr}$/J K^{-1}	25177.8	25171.9	25172.7	25184.9	25186.5	25185.1	25169.4	25179.1	25189.2
ΔT_{ad}/K	0.82525	0.77766	0.70102	0.78939	0.67834	0.63561	0.66443	0.87239	0.96168
ε_i/J K^{-1}	94.05	94.00	93.90	94.01	93.88	93.83	93.86	94.15	94.26
ε_f/J K^{-1}	92.55	92.48	92.42	92.48	92.39	92.35	92.38	92.62	92.73
$\Delta m(H_2O)$/g	–0.8	–2.2	–2.0	0.9	1.3	1.1	–2.8	–0.4	2.0
$-\Delta U$(IBP)^a/J	20854.61	19647.41	17711.27	19953.75	17147.59	16066.75	16784.50	22046.97	24313.44
ΔU(Melinex®)/J	1162.11	1334.36	1369.09	1260.34	1270.62	1245.72	1472.12	1565.32	1374.11
ΔU(fuse)/J	52.62	55.87	49.53	58.14	55.70	48.72	47.75	48.23	45.63
$\Delta U(HNO_3)$/J	28.66	23.28	21.25	21.85	21.25	18.27	20.18	31.52	37.01
$\Delta U(As_2O_3)$/J	332.75	308.44	272.92	314.52	269.72	244.45	259.16	343.57	378.12
ΔU(ign)/J	1.19	1.18	1.18	1.19	1.18	1.19	1.18	1.23	1.18
$\Delta U(H_2PtBr_4)$/J	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.19	0.22
ΔU(carbon)/J	11.88	0.00	0.00	0.00	0.00	0.00	0.00	6.60	0.00
ΔU_Σ/J	47.31	44.79	40.59	45.45	39.27	36.89	38.58	50.05	54.96
$-\Delta_c u^0$(compound)/J g^{-1}	21829.88	21863.55	21840.67	21863.82	21834.03	21850.53	21834.04	21854.39	21836.21

$\langle \Delta_c u^0 \rangle = -21845.2 \pm 4.4$ J g^{-1}

$^\alpha\Delta U$(IBP) contains ΔU(ign).

Labels mean: m(X) are the masses of X burnt in each experiment; $(\varepsilon_{cal})_{corr}$ is the energy equivalent of the calorimeter corrected for the amount of water used; ΔT_{ad} is the corrected temperature rise/variation of adiabatic temperature; ε_i and ε_f are the energy equivalents of contents in the initial state and in the final state, respectively; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 5222.5 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) and ΔU(Melinex®) are the energies of combustion of the fuse (cotton), and of Melinex®, respectively; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U(As_2O_3)$ is the energy of oxidation of the aqueous solution of As_2O_3; ΔU(ign) is the energy of ignition; $\Delta U(H_2PtBr_4)$ is the energy correction for the formation of the platinum complex; ΔU_Σ is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion.

Table 2 Standard (p^0=0.1 MPa) molar enthalpies of vaporization, at T=298.15 K determined by microcalorimetry for 3-bromoquinoline

T/K	m/mg	$\Delta^{\mathrm{g,T}}_{\mathrm{l,298.15\,K}}H_{\mathrm{m}}$/ kJ mol^{-1}	$\Delta^{\mathrm{T}}_{298.15\,\mathrm{K}}H^0_{\mathrm{m}}(g)$/ kJ mol^{-1}	$\Delta^{\mathrm{g}}_{\mathrm{l}}H^0_{\mathrm{m}}$(295.15 K)/ kJ mol^{-1}
371	12.846	82.46	12.21	70.25
371	10.054	84.99	12.21	72.78
373	8.322	78.56	12.54	66.02
372	10.327	86.68	12.37	74.31
373	11.945	82.27	12.54	69.73
371	9.459	83.55	12.21	71.34
$\langle\Delta^{\mathrm{g}}_{\mathrm{l}}H^0_{\mathrm{m}}(T=295.15\ \mathrm{K})\rangle$=70.7±2.3 kJ mol^{-1}				

Samples of about 8 to 12 mg of liquid compound, contained in a small thin glass capillary tube sealed at one end, and a blank capillary, were simultaneously dropped at room temperature into the hot reaction vessels in the Calvet high-temperature microcalorimeter (Setaram, Lyon, France), held at T=372 K, and were removed from the hot zone by vacuum evaporation. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within ±10 μg, into each of the twin calorimeter cells.

The observed enthalpies of vaporization $\Delta^{\mathrm{g,T}}_{\mathrm{l,298.15\,K}}H^0_{\mathrm{m}}$, were corrected to T=298.15 K using values of $\Delta^{\mathrm{T}}_{298.15\,\mathrm{K}}H^0_{\mathrm{m}}(g)$ estimated by a group-additivity method based on data of Stull *et al.* [24], where T is the temperature of the hot reaction vessel. The microcalorimeter was calibrated in situ for these measurements using the reported standard molar enthalpy of vaporization of decane [25].

Results and discussion

Detailed results for all the combustion experiments are given in Table 1, were $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to ε(calor), and ΔU_{Σ} is the correction to the standard state. The remaining terms have been previously described [16]. The individual values of massic energy of combustion, $\Delta_c u^0$, are referred to the combustion reaction:

$$C_9H_6NBr(l)+10.25O_2(g)+597.5H_2O(l)\rightarrow 9CO_2(g)+0.5N_2(g)+HBr\cdot 600H_2O(l) \quad (1)$$

in which reactants and products are in the thermodynamic standard states at T=298.15 K, with $HBr\cdot 600H_2O$(aq) as the bromine-containing product in the final state.

The derived standard molar energy of combustion is calculated as $\Delta_c U^0_{\mathrm{m}}(l)$= –4545.0±2.3 kJ mol^{-1}, leading to the standard molar enthalpy of combustion as $\Delta_c H^0_{\mathrm{m}}(l)$= –4546.9±2.3 kJ mol^{-1}, so the standard molar enthalpy of formation of 3-bromoquinoline, in the liquid state, is found to be $\Delta_f H^0_{\mathrm{m}}(l)$= 169.8±2.6 kJ mol^{-1}. In accordance with normal thermochemical practice [26, 27] 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 the auxiliary quantities used.

To derive $\Delta_f H^0_{\mathrm{m}}(l)$ from $\Delta_c H^0_{\mathrm{m}}$ the following standard molar enthalpies of formation at T=298.15 K were used: for $CO_2(g)$, –393.51±0.13 kJ mol^{-1} [28]; for $H_2O(l)$, –285.830±0.004 kJ mol^{-1} [28] and for $HBr\cdot 600H_2O(l)$, –120.924±0.005 kJ mol^{-1} [18, 28].

Individual results for the measurements of the enthalpy of vaporization are given in Table 2 with uncertainties of twice the standard deviation of the mean. From the experimental results, the standard molar enthalpies of vaporization at T=298.15 K, $\Delta^{\mathrm{g}}_{\mathrm{l}}H^0_{\mathrm{m}}(T$=298.15 K), were calculated from $\Delta^{372\,\mathrm{K}}_{298.15\,\mathrm{K}}H^0_{\mathrm{m}}(g)$=12.37 kJ mol^{-1} estimated by a group-additivity method, i.e., bromoquinoline= naphthalene+bromobenzene+pyridine–2benzene.

Combining the standard molar enthalpy of formation in the condensed phase, $\Delta_f H^0_{\mathrm{m}}(l)$, with the standard molar enthalpy of vaporization, $\Delta^{\mathrm{g}}_{\mathrm{l}}H^0_{\mathrm{m}}$(298.15 K), the standard molar enthalpy of formation in the gaseous state was derived as $\Delta_f H^0_{\mathrm{m}}(g)$= 240.5±3.5 kJ mol^{-1}.

Conclusions

From the literature values of the standard molar gas-phase enthalpies of formation for 3-bromopyridine, $\Delta_f H^0_{\mathrm{m}}(g)$=167.1±2.1 kJ mol^{-1} [29], pyridine, $\Delta_f H^0_{\mathrm{m}}(g)$=140.4±0.7 kJ mol^{-1} [25] and quinoline, $\Delta_f H^0_{\mathrm{m}}(g)$=200.54±0.94 kJ mol^{-1} [30], using the value obtained in this work for 3-bromoquinoline, the calculated enthalpic increments for the bromo substitution into the pyridine and into the pyridinic ring of quinoline, in the *meta* position, are 26.7±2.1 kJ mol^{-1} for pyridine and 40.0±3.6 kJ mol^{-1} for quinoline, differing by 13.3±4.2 kJ mol^{-1}, a value slightly higher than the limit 10 kJ mol^{-1} usually accepted by Cox [4] as a reasonable agreement between experimental and calculated values, showing that the Cox Scheme must be applied with some caution.

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References

1 http://www.patentstorm.us/patents/6541487.html (July 2006)
2 C. G. Stief, S. Ückert, A. J. Becker, M. C. Truss and U. Jonas, J. Urol., 159 (1998) 1390.
3 A. Küthe, H. Eckel, C. G. Stief, S. Ückert, W. G. Forssmann, U. Jonas and H. J. Mägert, Chem. Biol. Interact., 119–120 (1999) 593.
4 J. D. Cox, A Method for Estimating the Enthalpies of Formation of Benzene Derivatives in the Gas State, NPL Report CHEM 83, June 1978.
5 R. C. Weast, Ed., Handbook of Chemistry and Physics, 70th Ed., C. R. C. Press Inc. EUA 1989.
6 S. Sunner, Experimental Chemical Thermodynamics, S. Sunner and M. Månsson, Eds, Vol. 1, Pergamon Press, Oxford 1979, Chapter 2.
7 M. L. C. Vale, Graduation Thesis, Faculty of Science, University of Porto, 1989.
8 M. R. O. A. Silva, M. Sc. Thesis, Faculty of Science, University of Porto, 1993.
9 L. M. N. F. Santos, Ph.D. Thesis, University of Porto, 1995.
10 W. D. Good, D. W. Scott and G. Waddington, J. Phys. Chem., 60 (1956) 1080.
11 A. T. Hu, G. C. Sinke, M. Månsson and B. Ringnér, J. Chem. Thermodyn., 4 (1972) 283.
12 L. Bjellerup, Acta Chem. Scand., 11 (1957) 1761.
13 P. Sellers and S. Sunner, Acta Chem. Scand., 18 (1964) 202.
14 M. A. V Ribeiro da Silva, M. L. C. H. Ferrão and F. Jiye, J. Chem. Thermodyn., 26 (1994) 839.
15 H. A. Skinner and A. Snelson, Trans Faraday Soc., 56 (1960) 1776.
16 W. N. Hubbard, D. W. Scott and G. Waddington, Experimental Thermochemistry, F. D. Rossini, Ed., Vol. 1, Interscience, New York 1956, Chapter 5.
17 A. I. Vogel, Quantitative Inorganic Analysis, Longmans, London, 1978.
18 The NBS Tables of Chemical Thermodynamics Properties. J. Phys. Chem. Ref. Data, 11 (1982) Supplement No. 2.
19 E. W. Washburn, J. Rest. Bur. Stand., 10 (1933) 525.
20 L. G. Bjellerup, Experimental Thermochemistry, H. A. Skinner, Ed., Vol. 2, Interscience, New York 1962, Chapter 3.
21 M. E. Weiser, Pure Appl. Chem., 78 (2006) 2051.
22 F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, J. Organometal. Chem., 97 (1975) 221.
23 L. M. N. B. F. Santos, B. Schröder, O. O. P. Fernandes and M. A. V. Ribeiro da Silva, Thermochim. Acta, 415 (2004) 15.
24 D. R. Stull, E. F. Westrum and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York 1969.
25 J. B. Pedley, Thermochemical Data and Structures of Organic Compounds, Vol. 1, Thermodynamics Research Centre, College Station, TX 1994.
26 F. D. Rossini, Experimental Thermochemistry, F. D. Rossini, Ed., Vol. 1, Interscience, New York 1956, Chapter 14.
27 G. Olofsson, Combustion Calorimetry, S. Sunner, M. Månsson, Eds, Pergamon Press, Oxford 1979, Chapter 6.
28 J. D. Cox, D. D. Wagman and V. A. Medvedev, CODATA Key values for Thermodynamics, Hemisphere, New York 1989.
29 M. A. V Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 29 (1997) 1545.
30 W. V. Steele, D. V. Archer, R. D. Chirico, W. B. Collier, I. A. Hossenlopp, N. K. Smith and B. E. Gammon, J. Chem. Thermodyn., 20 (1088) 1233.

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