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The energetics of isomeric benzoxazine diones: isatoic anhydride revisited

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The standard ($p° = 0.1$ MPa) molar enthalpy of formation of crystalline 2*H*-1,3-benzoxazine-2,4(3*H*)dione was measured, at $T = 298.15$ K, by static bomb calorimetry and the standard molar enthalpy of sublimation, at $T = 298.15$ K, was obtained using Calvet microcalorimetry. These values were used to derive the standard molar enthalpy of formation in the gaseous phase, $T = 298.15$ K, of $-(401.0 \pm 3.5)$ kJ mol^{-1}. The standard molar enthalpy of sublimation of isatoic anhydride was recalculated, and our recommended experimental value for the standard molar enthalpy of formation in the gaseous phase, $T = 298.15$ K, is $-(406.2 \pm 3.4)$ kJ mol^{-1}. Density functional calculations for the two isomers 2*H*-1,3-benzoxazine-2,4(3*H*)dione and isatoic anhydride, in which the ring nitrogen and oxygen have been transposed, confirm the experimental evidence of nearly identical thermochemical stability for these isomers.

Introduction

Isatoic anhydride and its derivatives have numerous uses.[1,2] Derivatives of its ring nitrogen–oxygen switched isomer, 2*H*-1,3-benzoxazine-2,4(3*H*)dione likewise have uses such as analgesics.[3] Extending our earlier thermochemical study of isatoic anhydride,[4] in the present work, we report the standard molar enthalpy of formation of 2*H*-1,3-benzoxazine-2,4(3*H*)-dione in the gaseous phase, obtained from measurements of the standard molar energy of combustion using a static bomb calorimeter and from the value for the standard molar enthalpy of sublimation measured by Calvet microcalorimetry. Additionally, high-level density functional theory calculations using the B3LYP hybrid exchange–correlation energy functional have been performed for the two isomers. Both calorimetric experimental and quantum chemical theory show the two isomers to have nearly identical enthalpies of formation.

Experimental

The enthalpy and temperature of fusion of the crystalline 2*H*-1,3-benzoxazine-2,4(3*H*)dione was derived from the DSC experiments: $\Delta^{1}_{cr} H°_m (T_{fus}) = 28.63 \pm 1.37$ kJ mol^{-1}, at $T_{fus} = 500.49 \pm 0.64$ K. The uncertainty assigned to the results is the standard deviation of the mean of six independent runs.

The individual results of all seven combustion experiments for 2*H*-1,3-benzoxazine-2,4(3*H*)dione are given in Table 1, together with the mean value of the standard massic energy of combustion, $<\Delta_c u°>$, and its standard deviation. This parameter refers to the combustion reaction:

$$C_8H_5NO_3\,(cr) + 31/4\,O_2\,(g) \longrightarrow 8\,CO_2\,(g) + 5/2\,H_2O\,(l) + 1/2\,N_2\,(g) \quad (1)$$

The symbols in this table have the same meaning as in reference 5. As samples were ignited at $T = 298.15$ K,

$$\Delta U(\text{IBP}) = -\{\varepsilon_{cal} + \Delta m(H_2O)c_p(H_2O, l) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\text{ign.}) \quad (2)$$

where ΔU(IBP) is the energy associated to the isothermal bomb process, ε_{cal} is the energy equivalent of the calorimeter without contents and corrected for the mass of water 3119.6 g, $\Delta m(H_2O)$ is the difference of added water from the previously mentioned standard value (3119.6 g), ε_f is the energy of the bomb contents after ignition, ΔT_{ad} is the adiabatic temperature raise (the calorimeter temperature change corrected for heat exchange and the work of stirring), and ΔU(ign.) is the energy of ignition.

Table 2 lists the derived standard molar energy and enthalpy of combustion, $\Delta_c U°_m$ (cr) and $\Delta_c H°_m$ (cr), and the standard molar enthalpy of formation for 1,3-benzoxazine-2,4(3*H*)dione in the crystalline phase, $\Delta_f H°_m$ (cr), at $T = 298.15$ K. In accordance with normal thermochemical practice,[6] the uncertainty assigned to the standard molar enthalpy of combustion is twice the overall standard deviation of the mean and includes the uncertainties in calibration and in the values of auxiliary quantities. To derive $\Delta_f H°_m$ (cr) from $\Delta_c H°_m$ (cr) the standard molar enthalpies of formation of H_2O(l) and CO_2(g), at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ mol^{-1}[7] and $-(393.51 \pm 0.13)$ kJ mol^{-1},[7] respectively, were used.

Measurements of the standard molar enthalpy of sublimation $\Delta^{g}_{cr} H°_m$, at $T = 298.15$ K, of 1,3-benzoxazine-2,4(3*H*)-dione and isatoic anhydride are given in Table 3 with uncertainties of twice the standard deviation of the mean. The derived standard molar enthalpies of formation, in both the crystalline and gaseous phases, are summarized in Table 4.

Theoretical results and discussion

Electronic energies, identified by the subscripts B3LYP/6-31G* and B3LYP/6-311G**, and the zero-point vibrational energies and thermal energy corrections are presented in Table 5, for

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Table 1 Experimental results of combustion of 2*H*-1,3-benzoxazine-2,4(3*H*)dione, at T = 298.15 K

$m(CO_2$, total)/g	1.70103	1.69667	1.72106	1.54576	1.76778	1.49704	1.56465
m(cpd)/g	0.78559	0.78354	0.79488	0.71356	0.81665	0.69102	0.72248
m(fuse)/g	0.00343	0.00346	0.00341	0.00354	0.00324	0.00350	0.00332
ΔT_{ad}/K	1.01253	1.00994	1.02497	0.92053	1.05420	0.89202	0.93261
ε_f/(J K^{-1})	15.63	15.62	15.64	15.53	15.66	15.50	15.53
$\Delta m(H_2O)$/g	0.0	0.1	0.2	0.1	0.0	−0.2	0.1
$-\Delta U$(IBP)/J	16220.17	16179.10	16420.33	14746.57	16887.79	14288.66	14940.13
$-\Delta U(HNO_3)$/J	30.69	30.51	31.16	28.18	32.66	26.98	29.49
$-\Delta U$(carbon)/J	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΔU(ign.)/J	1.20	1.19	1.20	1.19	1.19	1.20	1.17
$-\Delta U_\Sigma$/J	16.15	16.08	16.36	14.56	16.85	14.07	14.77
$-\Delta U$(fuse)/J	55.70	56.19	55.38	57.49	52.62	56.84	53.92
$-\Delta_c u°$/(J g^{-1})	20516.59	20517.55	20528.17	20525.73	20554.29	20535.98	20543.06
$<\Delta_c u°> = -(20531.6 \pm 5.2)$ J g^{-1}							

$m(CO_2$, total) is the total mass of CO_2 formed in the experiment; m (cpd) 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 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(IBP) includes ΔU(ign.); 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(carbon) is the energy correction for carbon formation; ΔU(ign.) is the energy of combustion of the fuse; ΔU_Σ is the energy correction to the standard state; $\Delta_c u°$ is the standard massic energy of combustion.

Table 2 Derived standard ($p°$ = 0.1 MPa) molar values in the crystalline phase, at T = 298.15 K (kJ mol^{-1})

Compound	$\Delta_c U°_m$ (cr)	$\Delta_c H°_m$ (cr)	$\Delta_f H°_m$ (cr)
2*H*-1,3-benzoxazine-2,4(3*H*)-dione	−(3349.4 ± 2.1)	−(3347.5 ± 2.1)	−(515.2 ± 2.3)
Isatoic anhydride[4]	−(3342.8 ± 1.6)	−(3340.9 ± 1.6)	−(521.8 ± 1.9)

Table 3 Standard ($p°$ = 0.1 MPa) molar enthalpies of sublimation, $\Delta^g_{cr}H°_m$ (298.15 K), at T = 298.15 K

Compound	No. of experiments	T/K	$\Delta^{g,T}_{cr,298.15\,K}H°_m$	$\Delta^T_{298.15\,K}H°_m$ (g)	$\Delta^g_{cr}H°_m$ (298.15 K)
2*H*-1,3-benzoxazine-2,4(3*H*)-dione	6	440	139.3 ± 2.7	25.1	114.2 ± 2.7
Isatoic anhydride	6	488	151.2 ± 2.8[4]	35.6	115.6 ± 2.8

Table 4 Derived standard ($p°$ = 0.1 MPa) molar enthalpies of formation, $\Delta_f H°_m$, and of sublimation, $\Delta^g_{cr}H°_m$, at T = 298.15 K (kJ·mol^{-1})

Compound	$\Delta_f H°_m$ (cr)	$\Delta^g_{cr}H°_m$	$\Delta_f H°_m$ (g)
2*H*-1,3-benzoxazine-2,4(3*H*)-dione	−(515.2 ± 2.3)	114.2 ± 2.7	−(401.0 ± 3.5)
Isatoic anhydride	−(521.8 ± 1.9)[4]	115.6 ± 2.8	−(406.2 ± 3.4)

Table 5 Calculated electronic energies (hartree), zero-point vibrational energies (kJ·mol^{-1}) and thermal corrections to T = 298.15 K (kJ·mol^{-1})

Compound	$E_{B3LYP/6\text{-}31G*}$	$E_{B3LYP/6\text{-}311G**}$	$E_{ZP/B3LYP/6\text{-}31G*}$	$E_{total/B3LYP/6\text{-}31G*}$ [a]
2*H*-1,3-benzoxazine-2,4(3*H*)dione	−588.32535391	−588.48686453	306.64	329.83
Isatoic anhydride[4]	−588.32334324	−588.48472548	305.78	329.26

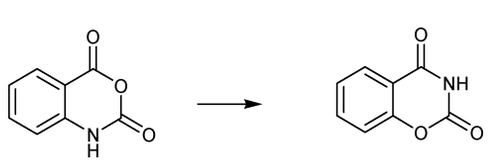
[a] E_{total} (T = 298.15 K) = $E_{trans} + E_{rot} + E_{ZP} + \Delta^{298.15\,K}_{0\,K}E_{vib}$

Table 6 Calculated reaction energies at T = 0 K and enthalpies at T = 298.15 K (kJ mol^{-1})

	$\Delta_r E_{T\,=\,0\,K}$		$\Delta_r H°_{T\,=\,298.15\,K}$		
	6-31G*	6-311G**	6-31G*	6-311G**	Experimental
Reaction 3	−5.3	−5.6	−4.7	−5.0	5.2 ± 5.0

the two isomers, 1,3-benzoxazine-2,4(3*H*)dione and isatoic anhydride; perhaps not surprisingly, the two sets of values are very similar for the two isomers.

In order to study the energetic stability of these systems we have considered the following isomerization reaction:



(3)

The resulting reaction energy at T = 0 K, and enthalpy at T = 298.15 K are presented together with the corresponding experimentally observed value in Table 6. Our experimental and calculational results are consistent with a small, if not zero, enthalpy of formation difference between the two isomers, 2*H*-1,3-benzoxazine-2,4(3*H*)dione and isatoic anhydride, *i.e.* we cannot ascertain from our studies which isomer is the more stable. A more thorough treatment of correlation energy is needed to more precisely discern the difference in the stability of the –NH–CO–O–CO– and –O–CO–NH–CO– functional groups.

Experimental

Material and purity control

The crystalline 2*H*-1,3-benzoxazine-2,4(3*H*)dione [2037-95-8] obtained commercially from Aldrich Chemical Co., with the minimum mass fraction purity of 0.999 (g.l.c.), was purified by vacuum sublimation. The average ratio of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample used, together with the standard deviation of the mean, was (1.0000 ± 0.0004). The density of the sample was estimated from the mass and the dimension of the pellet $\rho = 1.26$ g cm^{-3}.

The purity of this compound was also assessed by differential scanning calorimetry (DSC) using the fractional fusion technique.[8] The mass fraction of impurities found was less than 1×10^{-3}. DSC experiments were performed on a Setaram DSC 141 calorimeter using a heating rate of 3.33 ± 10^{-2} K s^{-1}. The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high purity reference materials (naphthalene, benzoic acid and indium) and its power scale was calibrated with high purity indium (mass fraction > 0.99999).[9] The recorded thermograms did not show any phase transitions between $T = 298$ K and the melting temperature of the samples contained in sealed stainless steel crucibles. The enthalpy and temperature of fusion were computed from the DSC thermograms.

Combustion calorimetry

The enthalpy of combustion was measured with a static bomb calorimeter. Since the apparatus and the technique have been described,[10,11] only a brief description will be given here. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190), having a massic energy of combustion, under certificate conditions, of $\Delta_c u = -(26435.1 \pm 3.5)$ J g^{-1}. Calibration experiments were carried out in oxygen at the pressure 3.04 MPa in the presence of 1.00 cm^3 of water added to the bomb. One set of seven calibration experiments was performed leading to the value of the energy equivalent of the calorimeter: $\varepsilon_{cal} = (16005.0 \pm 2.0)$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

For all experiments, the crystalline samples in the pellet form were ignited at $T = (298.150 \pm 0.001)$ K in oxygen at $p = 3.04$ MPa, with 1.00 cm^3 of water added to the bomb.

The electrical energy for ignition ΔU(ign.) was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, the specific energy of combustion is $\Delta_c u° = -16250$ J g^{-1},[12] a value previously confirmed in our laboratory. The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on -59.7 kJ mol^{-1},[13] for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l). The mass of compound, *m*(cpd), 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. An estimated pressure coefficient of specific 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, was assumed.[14] The standard massic energy of combustion, $\Delta_c u°$, was calculated by the procedure given by Hubbard *et al.*[5]

Microcalorimetry calvet

The standard molar enthalpy of sublimation of 2*H*-1,3-benzoxazine-2,4(3*H*)dione was measured using the "vacuum sublimation" drop microcalorimetric method.[15] Samples, about 3–5 mg of the crystalline compound, contained in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high temperature Calvet microcalorimeter (SETARAM HT 1000) held at a convenient temperature $T = 440$ K, and then removed from the hot zone by vacuum sublimation. For these measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpy of sublimation of naphthalene, (72.600 ± 0.600) kJ mol^{-1}.[16] The observed enthalpy of sublimation was corrected to $T = 298.15$ K using the equation:

$$\Delta_{298.15\,\mathrm{K}}^{T} H_{\mathrm{m}}^{\circ}(\mathrm{g}) = \int_{298.15\,\mathrm{K}}^{T} C_{\mathrm{p,m}}^{\mathrm{o}}(\mathrm{g})\mathrm{d}T \qquad (4)$$

where

$$C_{\mathrm{p,m}}^{\circ}(\mathrm{g}) = -0.000410T^2 + 0.721T - 32.139 \qquad (5)$$

was derived from statistical thermodynamics using the vibrational frequencies obtained from the B3LYP/6-31G* calculations. So correcting the sublimation enthalpy to $T = 298.15$ K, for 2*H*-1,3-benzoxazine-2,4(3*H*)dione we found a value of the sublimation enthalpy of (114.2 ± 2.7) kJ mol^{-1}. This value is very different from what we found and reported earlier for isatoic anhydride, (82.7 ± 2.8) kJ mol^{-1}.[4] In our earlier study we have used a group method to calculate the thermal corrections for the observed sublimation enthalpy for isatoic anhydride, (151.2 ± 2.8) kJ mol^{-1},[4] and an error was made in its application. In this work, using a procedure similar to the one we've used for 2*H*-1,3-benzoxazine-2,4(3*H*)dione (eqn 4), and using the following equation:

$$C_{\mathrm{p,m}}^{\circ}(\mathrm{g}) = -0.000410T^2 + 0.718T - 29.757 \qquad (6)$$

which was also derived from statistical thermodynamics and the calculated vibrational frequencies at the B3LYP/6-31G* level, we find the value of (115.6 ± 2.8) kJ mol^{-1} for the standard molar enthalpy of sublimation of isatoic anhydride, in much better agreement, and in strong and embarrassing disagreement with our aforementioned published value. So we derive the new value of $-(406.2 \pm 3.4)$ kJ mol^{-1} for the enthalpy of formation of isatoic anhydride in the gas phase.

The molar masses used for the elements were those recommended by the IUPAC commission.[17]

Computational details

The equilibrium geometries of the two isomers were obtained through complete geometry optimization using the density functional theory (DFT) based on the Becke 3-parameter hybrid exchange[18] and Lee–Yang–Parr[19] correlation density functional (B3LYP) and two different atomic basis sets: 6-31G*[20] and 6-311G**.[21]

The obtained B3LYP/6-31G* geometries were characterized as true minima through construction and diagonalization of the Hessian matrices. The harmonic vibrational frequencies, after scaling by the factor 0.9614,[22] were used to correct the computed electronic energy values for zero point vibrational energies, as well as, translational, rotational and vibrational contributions to the enthalpy at $T = 298.15$ K. All B3LYP calculations were carried out using the UK version of program GAMESS.[23,24]

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23 GAMESS-UK is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel and P. Sherwood, with contributions from R. D. Amos, R. J. Buenker, H. J. J. van Dam, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R. J. Harrison, A. P. Rendell, V. R. Saunders, A. J. Stone and A. H. de Vries. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler and J. Wendoloski, NRCC Software Catalog, vol. 1, program no. QG01 (GAMESS) 1980.
24 The DFT module within GAMESS-UK was developed by Dr. P. Young under the auspices of EPSRC's Collaborative Computacional Project No. 1 (CCP1) (1995–1997).