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Energetic studies of two oxygen heterocyclic compounds Xanthone and tetrahydro-γ-pyrone

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Abstract The present work reports an experimental thermochemical study supported by state of the art calculations of two heterocyclic compounds containing oxygen in the ring: xanthone and tetrahydro-γ-pyrone. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed phase, at $T = 298.15$ K, were derived from the measurements of the standard molar energies of combustion in oxygen atmosphere, using a static bomb calorimeter. The standard molar enthalpies of sublimation or vaporization, at $T = 298.15$ K, of the title compounds were obtained from Calvet microcalorimetry measurements. These values were used to derive the standard enthalpies of formation of the compounds in the gas-phase at the same temperature, which were compared with estimated data from G3(MP2)//B3LYP computations.

Keywords Calvet microcalorimetry · Combustion calorimetry · Enthalpy of formation · Enthalpies of transition · G3(MP2)//B3LYP calculations · Heat capacities

Introduction

Polycyclic compounds built from two benzenic rings fused to a central heteroatomic hexagonal or pentagonal ring (containing oxygen, nitrogen or sulfur) are important scaffolds in Chemistry, but with scarce information available in the literature regarding their thermodynamic properties. One of the goals of our research is the evaluation of the energetic effects introduced upon the substitution of the oxygen heteroatom by sulfur, as well as the influence of the chemical vicinity (insertion of *R* groups into the aromatic rings) in the structure and stability of the correspondent chemical species. In a quick search at the NIST Chemistry WebBook [1]—a large database containing, among other properties, the values of the standard molar enthalpies of formation of organic and inorganic compounds—it is possible to find several conflicting experimental results for the class of polycyclic heteroatomic compounds referred above. The wide dispersion of the values of the standard molar enthalpies of formation in the gaseous state, $\Delta_f H_m^o$ (g), for some of those backbone compounds (compounds without *R* groups), justifies our motivation to confirm their accuracy, since their enthalpies of formation will be the soil for a reliable database aiming predicting schemes for the characterization of the energetic behavior of related compounds. Therefore, the first stage in our study passes by the determination of the standard molar enthalpies of formation of the backbone compounds, by complementary experimental and computational studies.

On the progress of our study, we realized the importance of xanthone (dibenzo-γ-pyrone) **1**, a compound whose framework appears in a large number of more complex molecules. The chemical nature and position of the substituents in the aromatic rings, can lead to multiple

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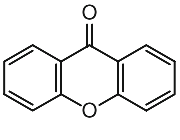
biological and pharmacological activities, based on their diverse structures; anti-hypertensive, anti-oxidative, anti-bacterial, anti-viral, anti-inflammatory, anti-thrombotic and anti-cancer activities have been reported [2–8]. Values for the $\Delta_f H_m^o$ (g) of this compound are already available in the literature [9, 10]; the difference between the two published results, led us to perform a new experimental study supported by computational work. The $\Delta_f H_m^o$ (g) of a monocyclic compound, tetrahydro-γ-pyrone (tetrahydro-4*H*-pyran-4-one) **2**, was also determined in this work. The structure of this compound is similar to the central ring of xanthone. The knowledge of the $\Delta_f H_m^o$ (g) of this monocyclic compound is important for the present computational thermochemical studies based on substitution or isodesmic reactions.



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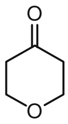

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The values of the $\Delta_f H_m^o$ (g) for xanthone and tetrahydro-γ-pyrone were derived from their standard molar energies of combustion, $\Delta_c U_m^o$, measured by static bomb calorimetry, and the correspondent standard molar enthalpies of sublimation, $\Delta_{cr}^{g} H_m^o$, or vaporization, $\Delta_{l}^{g} H_m^o$ measured by Calvet microcalorimetry. The experimental results in the gas-phase are compared with computational data obtained with state of the art computational approaches.

Experimental details

Materials

The solid compound xanthone [CAS 90-47-1] and the liquid compound tetrahydro-γ-pyrone [CAS 29943-42-8] were obtained commercially from Aldrich Chemical Co., with pureness 99.7 and 98.5%, respectively.

Two different strategies were employed for the purification of the samples before the calorimetric studies: xanthone was purified by repeated sublimation under reduced pressure while tetrahydro-γ-pyrone was purified by repeated fractional distillation under reduced pressure. Control of the purity was made by gas-liquid cromatography (g.l.c.) and also by the percentage of carbon dioxide (CO_2) recovered during the combustion experiments. The average ratios of the mass of CO_2 recovered to that calculated from the mass of the sample, together with the standard deviation of the mean, were: xanthone (1.0002 ± 0.0003); tetrahydro-γ-pyrone (1.0003 ± 0.0003). The values of the densities used for xanthone and tetrahydro-γ-pyrone were, respectively, 1.391 g cm^{-3} [11] and 1.084 g cm^{-3} [12].

The compounds used in the calibrations of the calorimetric systems were benzoic acid, Standard Reference Material (SRM), supplied by National Bureau of Standard (NBS), anthracene (zone-refined, 99 +%) and decane (99 +%), both obtained from Aldrich Chemical Co.

Static bomb calorimetry

The massic energies of combustion of the compounds were measured using an isoperibol calorimeter equipped with a twin valve static bomb of internal volume equal to 0.290 dm^3. Details of the apparatus and of the procedure were previously described [13–15] so only a brief description of the calibration and some details of the experiments will be given here.

The energy equivalent of the calorimeter ε(cal) was determined from the combustion of benzoic acid, NBS SRM 39j, the certificate of which gave the massic energy of combustion $\Delta_c u = -(26434 \pm 3)$ J g^{-1} under standard bomb conditions. Calibration experiments were carried out in oxygen, at a pressure of 3.04 MPa (previously flushed) with 1.00 cm^3 of desionized water added to the bomb. One set of eight calibration experiments was performed leading to the value of the energy equivalent of the calorimeter $\varepsilon(\text{cal}) = 15546.3 \pm 1.3$ J K^{-1} (where the uncertainty quoted is the standard deviation of the mean) for an average mass of water added to the calorimeter of 2900.0 g.

For the combustion experiments, the solid samples of xanthone were pressed into pellets while the liquid samples of tetrahydro-γ-pyrone were enclosed into polyester bags made from Melinex, using the technique described by Skinner and Snelson [16]. The combustion bomb was flushed and filled with oxygen until reaching a pressure of 3.04 MPa. The energy of reaction was always referred to the initial temperature of 298.15 K, so the ignitions of the samples were made at $T = (298.150 \pm 0.001$ K).

After the calorimetric measurements the combustion products were analyzed. The CO_2 formed was collected in absorption tubes [17]. The nitric acid formed, due to the presence of nitrogen residues in the oxygen used in the filling of the bomb, was determined by titration and the respective correction was based on -59.7 kJ mol^{-1} (the molar energy of formation for 0.1 mol dm^{-3} HNO_3 (aq) from N_2 (g), O_2 (g) and H_2O (l) [18]). The value for the pressure coefficient of specific energy $(\partial u/\partial p)_T$, was assumed to be -0.2 J g^{-1} MPa^{-1}, at $T = 298.15$ K, a typical value for most organic compounds [19].

The standard massic energies of combustion of the compounds, $\Delta_c u^o$, were calculated according to the procedure given by Hubbard et al. [20].

Calvet microcalorimetry

The $\Delta_{cr}^{g}H_{m}^{o}$ for xanthone and $\Delta_{l}^{g}H_{m}^{o}$ for tetrahydro-γ-pyrone were measured by the high vacuum drop-microcalorimetric technique. The technique was previously described by Skinner et al. [21] and Ribeiro da Silva et al. [22] for the study of solids and liquids, respectively.

The measurements were performed with a Calvet high-temperature microcalorimeter (Setaram HT1000) with the vacuum promoted by a rotary vacuum pump and a vapor diffusion pump. The details of the apparatus and of the technique are in the literature [23]. The microcalorimeter was calibrated in situ at different temperatures, using recommended reference materials for sublimation and vaporization enthalpies measurements [24]. For the sublimation enthalpy measurements at $T = 417$ K, the primary reference material used was anthracene. At this temperature the value of the calibration constant of the microcalorimeter was obtained as the average of six independent calibration experiments, $k_{cal} = 0.995 \pm 0.018$ using the reported standard molar enthalpy, at $T = 298.15$ K, $\Delta_{cr}^{g}H_{m}^{o}$ (anthracene) $= 100.4 \pm 0.4$ kJ mol^{-1} [25]. For the vaporization enthalpy experiments of tetrahydro-γ-pyrone, the calibration constant of the microcalorimeter at $T = 315$ K, determined using decane, was $k_{cal} = 1.018 \pm 0.005$, obtained as the average of six independent calibration experiments using the reported standard molar enthalpy, at $T = 298.15$ K, $\Delta_{l}^{g}H_{m}^{o}$ (decane) $= 51.42 \pm 0.21$ kJ mol^{-1}[24].

The relative atomic masses used were those recommended by the IUPAC commission in 2005 [26].

Computational details

The standard *ab initio* molecular orbital calculations for xanthone and tetrahydro-γ-pyrone were performed with the Gaussian-03 suite of programs [27]. The computational methodology employed was the G3(MP2)//B3LYP approach [28]. In this approach, the molecular geometry is optimized with the hybrid B3LYP method and the atomic electron density was described with the 6-31G(d) basis set. The B3LYP/6-31G(d) equilibrium structure is then used to calculate the vibrational frequencies. The zero-point energy, E(ZPE), was scaled by a factor of 0.96 to take account for known deficiencies at this level. Then, single point electronic energy calculations are performed using higher levels of electronic structure theory, quadratic configuration interaction [QCISD(T)] and the 2nd-order Moller-Plesset (MP2) with the 6-31G(d) and GTMP2Large basis sets, respectively. The energies (including the ZPE) computed at $T = 0$ K were thermally corrected for $T = 298.15$ K by introducing the vibrational term computed at the B3LYP/6-31G(d) and the translational, rotational and pV terms. The $\Delta_{f}H_{m}^{o}$ (g) for xanthone and tetrahydro-γ-pyrone were estimated from the calculated enthalpies of several gas-phase working reactions, c.f. Eqs. 1–5, using the values of $\Delta_{f}H_{m}^{o}$ (g) available in the literature for all the other species. It must be noticed that some of these reactions are not isodesmic and that some errors due to the consideration of different bonds in the reactants and in the products may not be compensated.

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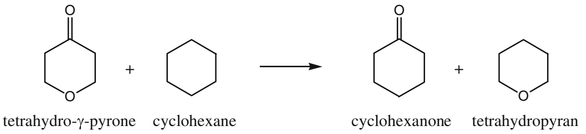

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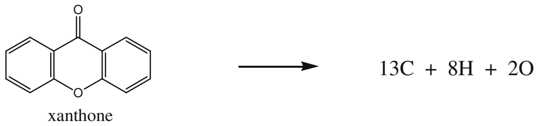

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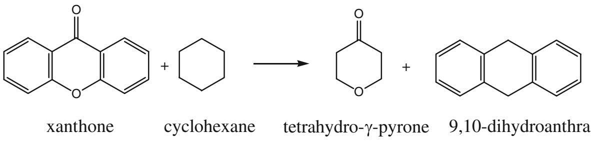

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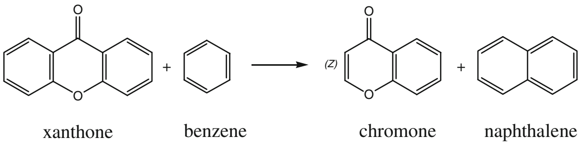

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Results

Experimental results

In the experiments of combustion with xanthone and tetrahydro-γ-pyrone, the compounds in the presence of oxygen are converted into carbon dioxide and water according to the reactions described by Eqs. 6 and 7, respectively.

$$C_{13}H_{8}O_{2}\,(cr) + 14\,O_{2}\,(g) \rightarrow 13\,CO_{2}\,(g) + 4H_{2}O\,(l) \tag{6}$$

$$C_{5}H_{8}O_{2}\,(l) + 6\,O_{2}\,(g) \rightarrow 5\,CO_{2}\,(g) + 4H_{2}O\,(l) \tag{7}$$

The results for typical combustion experiments for xanthone and tetrahydro-γ-pyrone and the individual values of $\Delta_{c}u^{\circ}$, together with the mean and the standard deviation of the mean, for each compound are given as Supporting Information. The energy associated to the isothermal bomb process, ΔU(IBP), was calculated through Eq. 8, where

ΔT_{ad} is the temperature rise corrected for the heat exchange and the work of stirring, $\Delta m(\mathrm{H_2O})$ represents the deviation of the mass of water added to the calorimeter from 2900.0 g, the water assigned to ε(cal), ε_{f} is the energy equivalent of the contents in the final state, $\Delta U(\mathrm{ign})$ is the electric energy for the ignition and c_p ($\mathrm{H_2O}$, l) is the massic heat capacity at constant pressure for liquid water.

$$\Delta U(\mathrm{IBP}) = -\left\{\varepsilon(\mathrm{cal}) + \Delta m\,(\mathrm{H_2O})\,c_p(\mathrm{H_2O, l}) + \varepsilon_{\mathrm{f}}\right\}\Delta T_{\mathrm{ad}} + \Delta U(\mathrm{ign}) \quad (8)$$

Table 1 lists the mean value of the massic energies of combustions, $\Delta_{\mathrm{c}}u^{\mathrm{o}}$, and the derived values of standard molar energies and enthalpies, respectively, $\Delta_{\mathrm{c}}U^{\mathrm{o}}_{\mathrm{m}}$ and $\Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}}$, of the reactions described by Eqs. 6 and 7 as well as the standard molar enthalpy of formation, $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$, of the compounds. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and of formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ from $\Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}}$, the standard molar enthalpies of formation of $\mathrm{H_2O}$ (l), $\mathrm{CO_2}$ (g), at $T =$ 298.15 K, respectively, -285.830 ± 0.042 kJ mol^{-1} [29] and -393.51 ± 0.13 kJ mol^{-1} [29] were used.

Results of microcalorimetric measurements of the enthalpies of sublimation and vaporization of xanthone and tetrahydro-γ-pyrone, respectively, are given in Table 2. The observed enthalpies of sublimation and vaporization, at experimental temperature T, $\Delta^{\mathrm{g},T}_{\mathrm{cr,l,298.15K}}H^{\mathrm{o}}_{\mathrm{m}}$, correspondent to the mean of six experiments with uncertainties given by their standard deviations, were corrected to $T = 298.15$ K (Eq. 9), being the molar heat capacities in the gaseous phase for tetrahydro-γ-pyrone (Eq. 10) and xanthone (Eq. 11) derived from statistical thermodynamics, by the use of the vibrational frequencies from the DFT calculations (B3LYP) with 6-31G(d) basis set [30]. The molar heat capacity in the gaseous phase for both compounds between 100 and 1000 K are given as Supporting Information.

$$\Delta^{T}_{298.15\,\mathrm{K}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{g}) = \int_{298.15\,\mathrm{K}}^{T} C^{\mathrm{o}}_{p,\mathrm{m}}(\mathrm{g})\,\mathrm{d}T \quad (9)$$

$$\begin{aligned} C^{\mathrm{o}}_{p,\mathrm{m}}(\mathrm{g})/(\mathrm{J\,mol^{-1}\,K^{-1}}) = &-1.14022\times10^{-7}(T/\mathrm{K})^3 \\ &+ 3.26671\times10^{-5}(T/\mathrm{K})^2 \\ &+ 3.32627\times10^{-1}(T/\mathrm{K}) \\ &- 11.9698 \\ &\left(\mathrm{R}^2 = 0.9992\right) \end{aligned} \quad (10)$$

$$\begin{aligned} C^{\mathrm{o}}_{p,\mathrm{m}}(\mathrm{g})/(\mathrm{J\,mol^{-1}\,K^{-1}}) = &-4.16969\times10^{-9}(T/\mathrm{K})^3 \\ &- 3.62486\times10^{-4}(T/\mathrm{K})^2 \\ &+ 8.18651\times10^{-1}(T/\mathrm{K}) \\ &- 15.7630 \\ &\left(\mathrm{R}^2 = 0.9993\right) \end{aligned} \quad (11)$$

The uncertainties associated to the standard enthalpies of sublimation and vaporization, at $T = 298.15$ K, are twice the standard deviations of the mean and include the uncertainties associated with the calibration procedure and the molar heat capacities for each compound in the gaseous state.

The derived standard molar enthalpies of sublimation, vaporization and formation, in crystalline, liquid and gaseous phases, at $T = 298.15$ K, are summarized in Table 3.

Computational results

The bond distances and angles of the structures optimized at the B3LYP/6-31G(d) level of theory for tetrahydro-γ-pyrone and xanthone are given as Supporting Information. Both molecules have a plane of symmetry that bisects the molecules through the carbonyl group and the oxygen of the ring. A chair conformation is predicted for tetrahydro-

Table 1 Derived standard ($p^{\circ} = 0.1$ MPa) massic and molar values in the solid and liquid phases, at $T = 298.15$ K

Compound	$\Delta_{\mathrm{c}}u^{\mathrm{o}}$/J g^{-1}	$\Delta_{\mathrm{c}}U^{\mathrm{o}}_{\mathrm{m}}$/kJ mol^{-1}	$\Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}}$/kJ mol^{-1}	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$/kJ mol^{-1}
Tetrahydro-γ-pyrone (l)	−27258 ± 12	−2729.0 ± 2.5	−2731.5 ± 2.5	−379.4 ± 2.6
Xanthone (cr)	−30885.7 ± 8.6	−6059.8 ± 3.6	−6062.3 ± 3.6	−196.7 ± 4.0

Table 2 Standard ($p^{\circ} = 0.1$ MPa) molar enthalpy of sublimation, $\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}$, and vaporization, $\Delta^{\mathrm{g}}_{\mathrm{l}}H^{\mathrm{o}}_{\mathrm{m}}$, for xanthone and tetrahydro-γ-pyrone, respectively, at $T = 298.15$ K, determined by Calvet microcalorimetry

Compound	Number of experiments	T/K	$\Delta^{\mathrm{g},T}_{\mathrm{cr,l,298.15K}}H^{\mathrm{o}}_{\mathrm{m}}$/kJ mol^{-1}	$\Delta^{T}_{298.15\mathrm{K}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{g})$/kJ mol^{-1}	$\Delta^{\mathrm{g}}_{\mathrm{cr,l}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\mathrm{K})$/kJ mol^{-1}
Tetrahydro-γ-pyrone (l)	6	315	52.5 ± 0.1	1.843 ± 0.005	50.7 ± 0.3
Xanthone (cr)	6	417	130.1 ± 1.3	27.424 ± 0.007	102.7 ± 2.3

Table 3 Derived standard ($p^\circ = 0.1$ MPa) molar enthalpies of sublimation, vaporization and formation, in crystalline, liquid and gaseous phases, at $T = 298.15$ K, for tetrahydro-γ-pyrone and xanthone

Compound	$\Delta_f H_m^o$ (cr,l)/kJ mol^{-1}	$\Delta_{cr,l}^{g} H_m^o$/kJ mol^{-1}	$\Delta_f H_m^o$ (g)/kJ mol^{-1}
Tetrahydro-γ-pyrone (l)	−379.4 ± 2.6	50.7 ± 0.3	−328.7 ± 2.6
Xanthone (cr)	−196.7 ± 4.0	102.7 ± 2.3	−94.0 ± 4.6

Table 4 G3(MP2)//B3LYP gas-phase enthalpies of formation, at $T = 298.15$ K, for tetrahydro-γ-pyrone and xanthone

Compound	Reaction	$\Delta_f H_m^o$ (g)/kJ mol^{-1}
Tetrahydro-γ-pyrone	1	−324.3
	2	−323.3
Xanthone	3	−108.2
	4	−95.0
	5	−110.9[a]
	5	−88.5[b]

[a] Value estimated using $\Delta_f H_m^o$ (g) for chromone from ref. [10]

[b] Value estimated using $\Delta_f H_m^o$ (g) for chromone from ref. [32]

γ-pyrone while a totally planar geometry is determined for xanthone; furthermore, these compounds present C_s and C_{2v} symmetries, respectively. The molecular structure of gaseous xanthone from electron diffraction data has been determined in the past [31]. The experimental data (C_{2v} symmetry) compare satisfactorily with the B3LYP/6-31G(d) results.

The estimated enthalpies of formation in the gaseous phase, at $T = 298.15$ K, for both compounds are presented in Table 4 [32]. The values have been calculated with the G3(MP2)//B3LYP absolute enthalpies at $T = 298.15$ K for tetrahydro-γ-pyrone, xanthone and for the auxiliary species in the gas-phase working reactions described by Eqs. 1–5, which appear as Supporting Information. Experimental gas-phase enthalpies of formation at $T = 298.15$ K for the auxiliary compounds are also given as Supporting Information. As it can be seen in Table 4, the use of atomization and isodesmic reactions yield identical values for tetrahydro-γ-pyrone while a noticeable difference is found for xanthone when atomization and two different isodesmic reactions are employed.

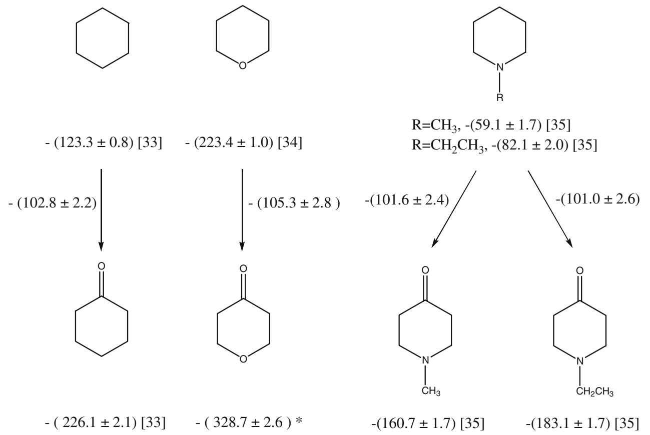
Discussion

The experimental and calculated $\Delta_f H_m^o$ (g), at $T = 298.15$ K, reported in the present work for tetrahydro-γ-pyrone and xanthone are listed in Table 5, together with other experimental values available in the literature for xanthone. The new experimental $\Delta_f H_m^o$ (g) for tetrahydro-γ-pyrone is in excellent agreement with the G3(MP2)//B3LYP calculated values. For xanthone the agreement between the new experimental and some calculated values is not so evident. On one hand, there is a significant difference between the estimated $\Delta_f H_m^o$ (g) of xanthone, using the atomization reaction described by Eq. 3, and the available experimental results. This difference may be related with the absence of thermochemical data for large molecules in the set of compounds used in the parameterization of the G3(MP2)//B3LYP methodology. On the other hand, the large difference found between the present experimental result and those calculated with reaction described by Eq. 5, is mostly probably due to inaccuracies in the experimental $\Delta_f H_m^o$ (g) for the auxiliary species considered in that reaction, in particular the value of the $\Delta_f H_m^o$ (g) for chromone; in fact, there are two experimental results for the latter compound available in the literature but they differ by more than 22 kJ mol^{-1} (c.f. Supporting Information). Finally, an excellent estimate is obtained when the working reaction described by Eq. 4 is used. This gives enhanced support to both experimental results determined in this work (xanthone and tetrahydro-γ-pyrone). It shows also that computational chemistry is able to provide accurate thermochemical data when appropriate reactions are used (reactions with reactants and products of reaction with similar bonds and with solid experimental $\Delta_f H_m^o$ (g) values).

As it was said above, two previous experimental $\Delta_f H_m^o$ (g) for xanthone were available in the literature (c.f. Table 5). Different strategies have been employed to reach those quantities from the corresponding enthalpies of formation in the crystalline state and of sublimation. Kim et al. [9] measured, by oxygen bomb calorimetry, the

Table 5 Derived standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the gaseous phases, at $T = 298.15$ K, for tetrahydro-γ-pyrone and xanthone

Compound	$\Delta_f H_m^o$ (g)/kJ mol^{-1}		
	Experimental	Calculated (equation)	Literature
Tetrahydro-γ-pyrone	−328.7 ± 2.6	−324.3 (1)	–
		−323.3 (2)	
Xanthone	−94.0 ± 4.6	−108.2 (3)	−79.2 ± 6.9 [9]
		−95.0 (4)	
		−110.9 (5)	−98.2 ± 3.6 [10]
		−88.5 (5)	



* This work.

Scheme 1 Enthalpic increments for the oxidation of some cyclic molecules (values in kJ mol^{-1})

energy of combustion of crystalline xanthone, deriving the correspondent enthalpy of formation, $\Delta_f H^o_m$ (cr) $= -191.5 \pm 2.7$ kJ mol^{-1}, at $T = 298.15$ K. The same authors have estimated the enthalpy of sublimation of xanthone, calculating the average of the enthalpy of sublimation values of related compounds, with similar molecular weights and structure (dibenzopyran and anthraquinone), which led to the value $\Delta^g_{cr} H^o_m = 112.3 \pm 6.3$ kJ mol^{-1}. The same properties were determined also by Sabbah and Watik [10], using a combustion calorimeter and a Tian-Calvet calorimeter, associated to an effusion cell. The values obtained by Sabbah and Watik [10] were $\Delta_f H^o_m$ (cr) $= -196.8 \pm 3.6$ kJ mol^{-1} and $\Delta^g_{cr} H^o_m = 98.57 \pm 0.36$ kJ mol^{-1}, at $T = 298.15$ K. Our experimental value, $\Delta_f H^o_m$ (g) $= -94.0 \pm 4.6$ kJ mol^{-1}, compares quite good with the result of Sabbah and Watik [10] (considering the intervals defined by the uncertainties associated with the experimental results) but differs by ~ 15 kJ mol^{-1} from the value estimated by Kim et al. [9]. As it can be seen, the most important source for such large difference is due to the estimated enthalpy of sublimation considered by Kim et al. [9].

The comparison of the enthalpic increments concerning the substitution of a –CH_2– group by a –C(=O)– group on cyclohexane, tetrahydropyran (*para* position relative to –O–) and 1-alkylpiperidine (*para* position relative to –N(R)–, R=CH_3, CH_2CH_3) are presented in Scheme (1). Identical increments are found for the insertion of oxygen atoms in cyclohexane and tetrahydropyran rings yielding cyclohexanone and tetrahydro-γ-pyrone, respectively, i.e., -102.8 ± 2.2 kJ mol^{-1} and -105.3 ± 2.8 kJ mol^{-1} [33, 34]. These increments are also very similar, within the intervals defined by the uncertainties associated with the gas-phase standard molar experimental enthalpies of formation, to the enthalpic increment (approx. -101 kJ mol^{-1}) obtained by Ribeiro da Silva et al. [35] for substitution of a –CH_2– group by a –C(=O)– group in position 4 of the 1-methyl and 1-ethyl-piperidine molecules, which presents also a chair configuration [36].

Final considerations

The standard molar enthalpies of formation in the gas-phase for tetrahydro-γ-pyrone and xanthone compounds were determined by experimental and computational approaches. The values coming from these two different approaches are in perfect agreement in the case of tetrahydro-γ-pyrone while important differences are found in the case of xanthone. These are attributed to possible inaccuracies in the experimental enthalpies of formation in the gas-phase of the auxiliary species considered since the computational approach used seems to provide very good structures and it is also able to provide very good thermochemical data for the separated tetrahydro-γ-pyrone and benzene fragments of xanthone. The experimental $\Delta_f H^o_m$ (g) for tetrahydro-γ-pyrone and xanthone are -328.7 ± 2.6 kJ mol^{-1} and -94.0 ± 4.6 kJ mol^{-1}, respectively.

The $\Delta_f H^o_m$ (g) for xanthone compares well with a previous experimental result due to Sabbah and Watik (-98.2 ± 3.6 kJ mol^{-1}) [10] but differs significantly from another value due to Kim et al. (-79.2 ± 6.9 kJ mol^{-1}) [9] since the latter authors derived their value considering an estimated enthalpy of sublimation.

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