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Experimental and computational thermochemistry of the isomers: Chromanone, 3-isochromanone, and dihydrocoumarin

M. Agostinha R. Matos [a,*], Clara C.S. Sousa [a], Victor M.F. Morais [a,b]

[a] Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências da, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal
[b] Instituto de Ciências Biomédicas Abel Salazar, ICBAS, Universidade do Porto, P-4099-003 Porto, Portugal

ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed state of chromanone, dihydrocoumarin, and 3-isochromanone were derived from the standard molar energies of combustion in oxygen at $T = 298.15$ K, measured by combustion calorimetry. Calvet microcalorimetry was used to derive the standard molar enthalpies of sublimation and vaporization.

Compound	$-\Delta_c U_m^0$(cr, l)/(kJ $\cdot$ mol^{-1})	$-\Delta_f H_m^0$(cr, l)/(kJ $\cdot$ mol^{-1})	$\Delta_{cr,l}^g H_m^0$/(kJ $\cdot$ mol^{-1})
Chromanone	4393.3 ± 1.6	289.1 ± 2.0	84.6 ± 1.3
Dihydrocoumarin	4364.6 ± 1.9	317.8 ± 2.2	69.9 ± 0.5
3-Isochromanone	4348.7 ± 1.4	333.7 ± 1.8	97.3 ± 1.4

From these values the standard molar enthalpies in the gaseous phase, at $T = 298.15$ K, were derived. Additionally estimates were performed of the enthalpies of formation of all the studied compounds in gas-phase, using DFT and other more accurate correlated calculations, together with appropriate isodesmic or homodesmic reactions. There is a reasonable agreement between computational and experimental results.

1. Introduction

As a class of compounds, chromones and chromanones have been attracting much attention among chemists in different fields.

Chromanone derivatives have been found to exhibit broad-spectrum biological activities, such as insecticidal, antifungal, antibacterial activities [1], and as perfuming ingredients [2]. 6-Methyl-4-chromanone was found to exhibit strong activity in inhibiting *in vitro* cell growth of human K562 cells [3].

Dihydrocoumarin derivatives have also applications in cosmetics; 7-methyl and 7-ethyldihydrocoumarin are used to obtain a coumarin type of odour [4].

In the present work, we report the standard molar enthalpies of formation of the three isomers in the gaseous phase, at $T = 298.15$ K. Our current results were obtained from measurements of combustion energies, at $T = 298.15$ K, using a static bomb calorimeter. The standard molar enthalpies of vaporization/sublimation were measured by Calvet microcalorimetry, at $T = 298.15$ K.
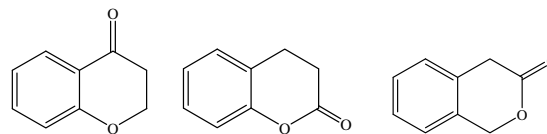
Chromanone   Dihydrocoumarin   3-isochromanone

Additional to the experimental thermochemical work, we present estimates of the enthalpies of formation of all the compounds studied in gas-phase, using DFT and also other more accurate composite correlated calculations together with appropriate isodesmic or homodesmic reactions.

2. Experimental

2.1. Materials and DSC

All the compounds were commercial products from Aldrich Chemical Co., chromanone [CAS 491-37-2], dihydrocoumarin [CAS 119-84-6], 3-isochromanone [CAS 4385-35-7]. All the samples were purified by repeated distillation or sublimation under

* Corresponding author. Tel.: +351 22 0402 517; fax: +351 22 0402 522.
E-mail address: marmatos@fc.up.pt (M.A.R. Matos).

TABLE 1
Temperatures of fusion, T_{fus}, enthalpies of fusion, $\Delta_{cr}^{l}H_m^0(T_{fus})$, and mass fraction of impurities, x, of the studied benzodioxan derivatives

Compound	T_{fus}/K	$\Delta_{cr}^{l}H_m^0(T_{fus})/(kJ \cdot mol^{-1})$	Purity
Chromanone	312.28 ± 0.05	16.72 ± 0.20	99.94 ± 0.04
3-Isochromanone	355.88 ± 0.07	18.27 ± 0.13	99.76 ± 0.43

reduced pressure before the experimental studies began. For the solid compounds, the purity (table 1) was derived from d.s.c. (Setaram DSC 141) analysis by a fractional fusion technique [5]. The samples, hermetically sealed in stainless steel crucibles, were heated at a rate of $1.67 \cdot 10^{-2} \, K \cdot s^{-1}$. The temperature scale of the calorimeter was calibrated by measuring the melting temperature of three high-purity reference materials (naphthalene, benzoic acid, and indium) [6] and its power scale was calibrated with high-purity indium (mass fraction > 0.99999). The recorded thermograms did not show any phase transition between $T = 298 \, K$ and the melting temperature of the compounds studied.

The mass fraction purity of the liquid compound, dihydrocoumarin, was evaluated as 0.9989 by gas–liquid chromatography (Agilent 4890 D chromatograph).

The purity of the samples was also confirmed through the carbon dioxide gravimetry results. The average ratios of the mass of carbon dioxide recovered after each combustion experiment to that calculated from the mass of sample, together with the standard deviation of the mean, were: chromanone (0.9994 ± 0.0002), dihydrocoumarin (0.9992 ± 0.01), 3-isochromanone (0.9997 ± 0.02). The density of the liquid dihydrocoumarin $1.169 \, g \cdot cm^{-3}$ was taken from literature [7] while the densities of the crystalline compounds were estimated, from the mass and the dimensions of samples in pellet form, as chromanone ($1.14 \, g \cdot cm^{-3}$), 3-isochromanone ($1.14 \, g \cdot cm^{-3}$).

2.2. Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter, using a twin valve bomb, type 1108 of Parr Instrument Company. The apparatus and technique have been described previously [8,9], so only a brief description is made here. For calibration of the bomb at two different stages of the experimental work (small changes in the calorimetric system were verified), we have used two different samples of benzoic acid thermochemical standard: BAS, BCS-CRM-190p and NBS 39j, whose massic energies of combustion under certificate conditions are respectively, $\Delta_c u = -(26435.1 \pm 3.5) \, J \cdot g^{-1}$ and $\Delta_c u = -(26434 \pm 3) \, J \cdot g^{-1}$. The calibration results were corrected to give the energy equivalent ε_{cal} corresponding to the average mass of water added to the calorimeter, 3119.6 g. From seven independent calibration experiments with the benzoic acid BAS, BCS-CRM-190p, $\varepsilon_{cal} = (16004.8 \pm 1.6) \, J \cdot K^{-1}$; from other six independent calibration experiments with the benzoic acid NBS 39j, $\varepsilon_{cal} = (16000.8 \pm 1.4)$, where the uncertainties quoted are the standard deviations of the mean. The first value of ε_{cal} was used in the combustion experiments of dihydrocoumarin while for chromanone and 3-isochromanone the second value was used.

The crystalline compounds were burnt in pellet form. Chromanone, due to its low melting point, and the liquid compound, dihydrocoumarin, were enclosed in polyester bags made of Melinex®, using the technique described by Skinner and Snelson [10] who determined the specific energy of combustion of dry Melinex® as $\Delta_c u^0 = -(22,902 \pm 5) \, J \cdot g^{-1}$. This value was confirmed in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported [10].

Combustion experiments were made in oxygen at $p = 3.04 \, MPa$, with $1.00 \, cm^3$ of water added to the bomb. The electrical energy for ignition, $\Delta U(ign)$, was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. As samples were ignited at $T = 298.15 \, K$,

$$\Delta U(IBP) = -\{\varepsilon_{cal} + \Delta m(H_2O) \cdot c_p(H_2O,l) + \varepsilon_f\}\Delta T_{ad} + \Delta U_{ign}, \quad (1)$$

where $\Delta U(IBP)$ is the energy associated to the isothermal bomb process, ε_f is the energy of the bomb contents after ignition and ΔT_{ad} is the adiabatic temperature raise calculated using the program LABTERMO [11]. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, the value of $-16250 \, J \cdot g^{-1}$ [12] was taken for the massic energy of combustion, $\Delta_c u^0$ (the value has been confirmed in our laboratory). The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on $-59.7 \, kJ \cdot mol^{-1}$ [13] for the molar energy of formation of $0.1 \, mol \cdot dm^{-3} \, HNO_3(aq)$ from N_2, O_2, and $H_2O(l)$. The mass of compound, m(compound), 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 and Melinex.

An estimated pressure coefficient of specific energy: $(\partial u / \partial p)_T = -0.2 \, J \cdot g^{-1} \cdot MPa^{-1}$ at $T = 298.15 \, K$, a typical value for most organic compounds, was assumed [14]. For each compound, the corrections to the standard state, ΔU_Σ, to derive the standard massic energy of combustion, $\Delta_c u^0$, were made by the procedure given by Hubbard *et al.* [15]. The atomic weights of the elements were those recommended by the IUPAC commission in 2005 [16].

2.3. Calvet microcalorimetry

The standard molar enthalpies of sublimation or vaporization were measured using the "vacuum sublimation" drop microcalorimetric method [17]. The microcalorimeter was calibrated *in situ* for these measurements using the reported enthalpy of sublimation of naphthalene [18] and of vaporization of *n*-decane [19].

Samples, of about 3 to 5 mg of the crystalline compounds and of 7 to 10 mg of the liquid compound, contained in a thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high temperature Calvet microcalorimeter (SETARAM HT 1000D) held at $T = 366 \, K$ for chromanone and 3-isochromanone and at $T = 362 \, K$ for dihydrocoumarin and then 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 into each of the twin calorimeter cells. From six independent experiments for each compound, a mean value was obtained for the observed standard molar enthalpy of sublimation/vaporization, $\Delta_{cr,l298.15K}^{g,T}H_m^0$, which was then corrected to $T = 298.15 \, K$, $\Delta_{298.15K}^{T}H_m^0(g)$, using the equation:

$$\Delta_{298.15K}^{T}H_m^0(g) = \int_{298.15K}^{T} C_{p,m}^0(g) \, dT, \quad (2)$$

where T is the temperature of the hot reaction vessel, $C_{p,m}^0(g)$ is the molar heat capacity of the compound in the gas-phase and was obtained from statistical thermodynamics using the vibrational frequencies obtained from the DFT calculations with the B3LYP functional and the 6-31G* basis set:

Chromanone

$$C_{p,m}^0(g)/(J \cdot mol^{-1} \cdot K^{-1}) = -0.000363(T/K)^2$$
$$+ 0.732(T/K) - 42.572. \quad (3)$$

Dihydrocoumarin

$$C_{p,m}^0(g)/(J \cdot mol^{-1} \cdot K^{-1}) = -0.000377(T/K)^2$$
$$+ 0.745(T/K) - 45.024. \quad (4)$$

3-Isochromanone

$$C_{p,m}^0(g)/(J \cdot mol^{-1} \cdot K^{-1}) = -0.000362(T/K)^2$$
$$+ 0.732(T/K) - 42.970. \quad (5)$$

3. Computational details

The geometries of all molecules have been fully optimized using density functional theory (DFT) with the Becke three-parameter hybrid exchange [20] and the Lee–Yang–Parr [21] correlation density functionals (B3LYP) and the Pople's split-valence 6-31G* extended basis set [22]. The optimum structures so obtained were further certified as true minima by constructing and diagonalizing the corresponding Cartesian Hessian matrix, this procedure providing also the harmonic vibrational frequencies which, after properly scaled by the recommended scaling factor 0.9614 [23] allow reliable calculations of the thermal corrections to the molecular energy. We have further refined the optimum structures by re-optimizing them using the same methodology with the Pople's split-valence 6-311G** extended basis set [24]. These final optimized structures were then used to perform single point DFT calculations with the cc-pVTZ basis set [25] and also energy calculations based on more accurate correlated computational techniques of the MCCM/3 suite [26,27].

All the geometry optimizations vibrational analysis and single point calculations have been performed using the UK version of program GAMESS [28,29]. The MCCM/3 series of calculations have been performed using the MLGAUSS program version 2.0 [30], which rely on the Gaussian 03 series of programs [31]. NBO analysis of the wave functions has been made by using the NBO5.0 module [41] inside the Gaussian 03 code.

4. Experimental results

The temperature of fusion of the crystalline compounds was measured using a differential scanning calorimeter. The results (observed in each case at the onset temperature of the calorimetric peak), T_{fus}, are presented in table 1 together with the enthalpies of fusion, at the temperatures of fusion, $\Delta_{cr}^l H_m^0(T_{fus})$, and the purity of the purified samples. Those values represent the mean values of six independent experiments on fresh samples and the uncertainties are twice the standard deviation of the mean.

Results for a typical combustion experiment of the three isomers are given in table 2. The values of the massic energy of combustion, $\Delta_c u^0$, refer to the combustion reaction:

$$C_9H_8O_2 \text{ (l)} + 10O_2 \text{ (g)} \rightarrow 9CO_2 \text{ (g)} + 4H_2O \text{ (l)}. \quad (6)$$
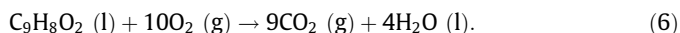
The individual results of all combustion experiments, together with the mean value and associated standard deviation, are given for each compound in table 3. Table 4 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for the compounds in the condensed phase, at $T = 298.15$ K. In accordance with normal thermochemical

TABLE 2
Typical combustion experiments, at $T = 298.15$ K

	Chromanone	Dihydrocoumarin	3-Isochromanone
$m(CO_2, \text{total})/g$	2.06418	1.71397	1.55805
$m(\text{cpd})/g$	0.72126	0.59460	0.58133
$m(\text{fuse})/g$	0.00271	0.00260	0.00243
$m(\text{melinex})/g$	0.05747	0.05248	–
$\Delta T_{ad}/K$	1.4216	1.1724	1.0687
$\varepsilon_f/(J \cdot K^{-1})$	16.10	15.75	15.66
$\Delta m(H_2O)/g$	0.0	0.0	0.0
$-\Delta U(\text{IBP})/J$	22768.97	18781.31	17115.94
$\Delta U(\text{fuse})/J$	44.01	42.22	39.46
$\Delta U(\text{melinex})/J$	1316.09	1201.86	–
$\Delta U(HNO_3)/J$	3.33	6.34	1.49
$\Delta U(\text{ign})/J$	0.66	1.18	0.85
$\Delta U_\Sigma/J$	15.37	12.52	11.12
$-\Delta_c u^0/(J \cdot g^{-1})$	29656.67	29462.45	29353.16

TABLE 3
Individual values of the massic energy of combustion, at $T = 298.15$ K

Chromanone	Dihydrocoumarin	3-Isochromanone
	$-\Delta_c u^0/(J \cdot g^{-1})$	
29638.82	29475.29	29354.05
29646.13	29471.80	29359.22
29656.67	29462.45	29353.16
29648.78	29456.27	29353.79
29661.77	29449.42	29338.40
29652.38	29460.69	29347.38
29661.84	29446.81	–
–	29442.85	–
	$-\langle \Delta_c u^0 \rangle/(J \cdot g^{-1})$	
29652.3 ± 3.2	29458.2 ± 4.1	29351.0 ± 3.0

practice, [32] 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 auxiliary quantities. To derive $\Delta_f H_m^0(cr, l)$ from $\Delta_c H_m^0(cr, l)$, the following standard molar enthalpies of formation, at $T = 298.15$ K, were used for $H_2O(l)$, $-(285.830 \pm 0.042)$ kJ $\cdot$ mol^{-1} [33]; $CO_2(g)$ and $-(393.51 \pm 0.13)$ kJ $\cdot$ mol^{-1} [33].

Measurements of the standard molar enthalpy of vaporization for dihydrocoumarin and of the standard molar enthalpies of sublimation for the crystalline compounds are given in table 5 with uncertainties of twice the standard deviation of the mean.

The derived standard molar enthalpies of formation, in both condensed and gaseous phases, at $T = 298.15$ K, are summarized in table 6.

5. Computational results and discussion

Each of the three isomeric chromanones has an optimum geometry consisting of a planar benzenic ring and a heterocyclic ring largely distorted from planarity. Planarity of the last ring is inhibited either by the angular strain within the sp^3 hybridized carbon atoms as well as the repulsion between contiguous –CH$_2$– groups. The hydrogen atoms of these fragments are, in fact, observed to adopt almost perfectly mutually staggered conformations for the chromanone and dihydrocoumarin isomers.

Total energies, identified by the subscripts B3LYP/6-311G**, B3LYP/cc-pVTZ, MC-UT/3 and MC-QCISD/3 as well as thermal corrections, TCE/6-31G*, are reported in table 6 for the studied compounds.

In order to estimate the enthalpies of formation of the systems from the calculated energies, we used the following set of

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TABLE 4
Derived standard (p° = 0.1 MPa) molar values, at T = 298.15 K

Compound	$-\Delta_c U_m^0/(kJ \cdot mol^{-1})$	$-\Delta_c H_m^0/(kJ \cdot mol^{-1})$	$-\Delta_f H_m^0(cr,l)/(kJ \cdot mol^{-1})$
Chromanone	4393.3 ± 1.6	4395.8 ± 1.6	289.1 ± 2.0
Dihydrocoumarin	4364.6 ± 1.9	4367.1 ± 1.9	317.8 ± 2.2
3-Isochromanone	4348.7 ± 1.4	4351.2 ± 1.4	333.7 ± 1.8

TABLE 5
Derived standard (p° = 0.1 MPa) molar enthalpies of formation at T = 298.15 K

Compound	$-\Delta_f H_m^0(cr,l)/kJ \cdot mol^{-1}$	$\Delta_{cr,l}^g H_m^0/(kJ \cdot mol^{-1})$	$-\Delta_f H_m^0(g)/(kJ \cdot mol^{-1})$
Chromanone	289.1 ± 2.0	84.6 ± 1.3	204.5 ± 2.4
Dihydrocoumarin	317.8 ± 2.2	69.9 ± 0.5	247.9 ± 2.3
3-Isochromanone	333.7 ± 1.8	97.3 ± 1.4	236.4 ± 2.3

TABLE 6
DFT electronic energies and thermal corrections to T = 298.15 K

Compound	$E_{B3LYP/6-311G^{**}}$	$E_{B3LYP/cc-pVTZ}$	$E_{MC-UT/3}$	$E_{MCQCISD/3}$	$TCE_{B3LYP/6-31G^*}$
Chromanone	−498.354741	−498.407293	−497.567733	−497.573964	0.154020
Dyhidrocoumarin	−498.370265	−498.423653	−497.584987	−497.591277	0.153806
3-Isochromanone	−498.364595	−498.418425	−497.580536	−497.586984	0.154028
α-Tetralone	−462.447184	−462.494829	−461.685403	−461.689668	0.177571
β-Tetralone	−462.440538	−462.489121	−461.681082	−461.685189	0.176749
1,4-Benzodioxan	−460.218270	−460.268935	−459.499477	−459.506267	0.148055
Tetralin	−388.407099	−388.447653	−387.736796	−387.739867	0.195113
Chromane	−424.315176	−424.360704	−423.620064	−423.625009	0.171603
Isochromane	−424.306671	−424.352605	−423.613636	−423.618520	0.171648
Pyran	−271.848229	−271.876181	−271.422446	−271.424958	0.147139
Cyclohexane	−235.947115	−235.969805	−235.543802	−235.544528	0.170406
Cyclohexanone	−309.979678	−310.010501	−309.487651	−309.489479	0.152520
Pyranone	−345.902757	−345.939006	−345.386061	−345.390108	0.129600

All energies are in a.u. (1 E_H = 2625.50184 kJ · mol^{-1}).
$TCE_{B3LYP/6-31G^*} = E_{trans} + E_{rot} + E_{zp} + \Delta_{0K}^{298.15 K} E_{vib}$.

TABLE 7
Theoretical estimates of the standard enthalpies of formation in the gas-phase at T = 298.15 K of 1,4-benzodioxanes

Compound	R	$-\Delta_f H_m^0(g)/kJ \cdot mol^{-1}$				
		6-311G**	cc-pVTZ	MC-UT/3	MC-QCISD/3	Exp.
Chromanone	IA	202.9	202.3	198.8	199.2	204.5 ± 2.4
	IB	202.4	202.2	201.3	201.6	
	IC	213.4	212.5	206.2	206.7	
	ID	204.4	201.5	196.0	196.5	
	AT	110.1	152.9	192.0	192.1	
Dihydrocoumarin	IIA	239.4	238.6	233.8	234.7	247.9 ± 2.3
	IIB	239.0	238.5	236.3	237.1	
	IIC	250.0	248.8	241.2	242.2	
	IID	245.7	245.0	241.9	242.5	
	IIE	251.4	249.5	247.2	246.9	
	AT	151.4	196.5	237.9	238.1	
3-Isochromanone	IIIA	226.6	226.3	221.7	223.1	236.4 ± 2.3
	IIIB	234.5	234.5	228.9	230.4	
	IIIC	233.4	232.8	227.3	228.5	
	IIID	235.9	235.2	234.9	235.1	
	AT	135.9	182.2	225.6	226.2	

AT-atomization reaction.

homodesmic reactions involving auxiliary systems whose thermochemical properties are well established experimentally [34–37].

The optimum geometries, the energies and the thermal corrections for all the auxiliary molecules have also been obtained using the same procedures as described above.

(IA)

(IB)

(IC)

(ID)

(IIA)

(IIB)

(IIC)

(IID)

(IIE)

(IIIA)

(IIIB)

(IIIC)

(IIID)
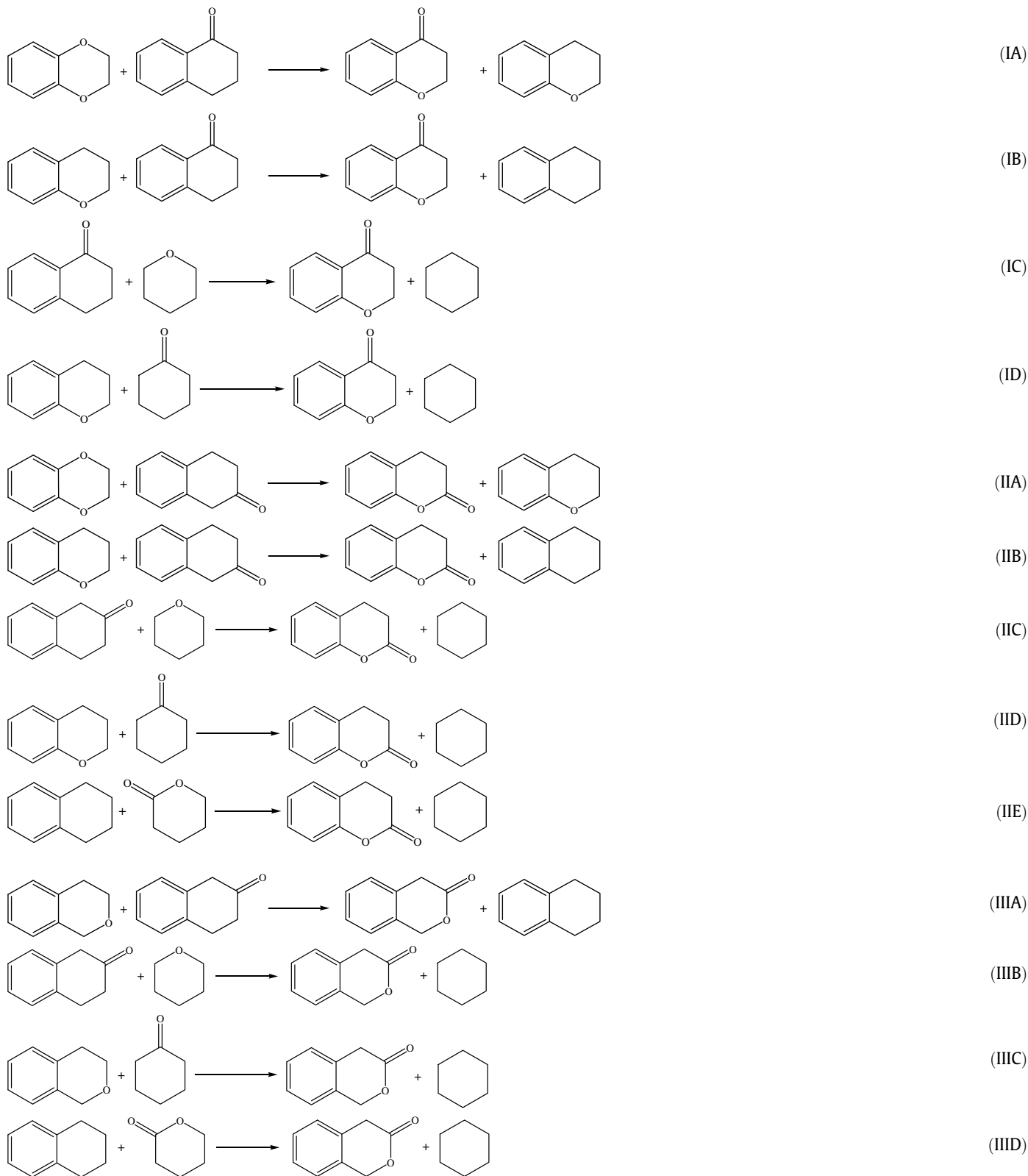
The estimated values of molar enthalpies of formation in the gaseous phase obtained by DFT calculations and MCCM/3 methods for the compounds are presented in table 7, for all reactions used. We can observe from that table a good agreement between our computational estimates and the experimental data, with almost

no significant difference between the DFT and the most accurate correlated MC-UT/3 and MC-QCISD/3 results. This is perhaps an indication of the adequacy of the chosen homodesmotic reactions. Differences between the two sets of calculations become apparent when we consider the estimates of the enthalpies of formation

obtained from atomization reactions. Even though we get acceptable results from the MC-UT/3 and MC-QCISD/3 energies, with deviations not exceeding 12.5 kJ · mol^{-1}, the estimates obtained from the more modest B3LYP energies become clearly unacceptable, since the associated errors can exceed 50 kJ · mol^{-1} for the B3LYP-ccPVTZ results and are even worst for the B3LYP-6-311G** ones. The experimentally observed stability ordering is well described by all our calculations which correctly predict dihydrocoumarin to be the most stable isomer, followed by 3-isochromanone (about 12 kJ · mol^{-1} less stable) and by chromanone (about 44 kJ · mol^{-1} more unstable). Thus, we recognize that those isomers which are more stabilized involve the O=C–O fragment. This behaviour is likely to be understood from the interactions involving electron delocalization of the lone electronic pairs of the oxygen atoms. We can quantitatively probe such interactions through an analysis of the wave functions in the framework of Natural Bond Orbital (NBO) theory [38–41], according to which, the electronic population should be distributed over a set of localized one-centre ("lone-pair") and two-centre ("bond") orbitals. This localized description closely mimics a classical Lewis type picture of the electronic system, while delocalization effects are evidenced by small occupancies of the set of anti-bonding orbitals. The stabilizing effect of such delocalization interactions can be quantitatively obtained as second-order perturbative estimates of the corresponding bonding–anti-bonding interactions. By doing so, we were able to identify the leading donor–acceptor interactions which are responsible for the different stabilities of the chromanone isomers as being those involving the π lone-electronic pair of the ring oxygen and the anti-bonding π*(C=O), which contributes with a stabilization energy of about 36 kcal · mol^{-1} and 43 kcal · mol^{-1}, respectively for dihydrocoumarin and for 3-isochromanone, and the π lone-electronic pair of the carbonyl oxygen and the anti-bonding σ*(C–O) involving the carbon atom of the same group and the other oxygen atom, contributing with 36 kcal · mol^{-1} and 34 kcal · mol^{-1}, respectively for dihydrocoumarin and for 3-isochromanone. Note that neither of the above interactions is allowed in chromanone. The other important interaction justifying differences in stability involve electronic delocalization from the π lone-electronic pair of the ring oxygen to the closer anti-bonding π*(C=C) of the benzenic ring. This interaction, which is absent in 3-isochromanone, contributes a stabilization of about 22 kcal · mol^{-1} and 28 kcal · mol^{-1}, respectively for dihydrocoumarin and chromanone.

6. Conclusions

In this paper, we have reported experimental measurements of the standard molar energies of combustion of chromanone, dihydrocoumarin, and 3-isochromanone in oxygen at T = 298.15 K, obtained by combustion calorimetry, which, together with the corresponding standard molar enthalpies of sublimation and vaporization, obtained from Calvet microcalorimetry, provided the experimental estimates of their standard molar enthalpies of formation in the gaseous phase. Calculations conducted at the DFT/B3LYP and at more accurate correlated levels provided also reliable estimates of the thermochemical parameters of the title species. The differences in accuracy between both sets of computational results become evident when we consider (non-isodesmic) atomization reactions instead of the more restrictive homodesmotic reactions. Indeed, in spite of both sets of calculations being equally appropriate in describing the energetics of the latter reactions, only the correlated calculations relying on the procedures of the MCCM/3 [26,27] suite provided acceptable descriptions of the energetics of atomization reactions.

References

[1] P. Zhao, J. Li, G. Yang, Bioorg. Med. Chem. 15 (2007) 1888–1895.
[2] http://www.wipo.int/pctdb/en/wo.jsp?IA=WO2006046159&wo=2006046159 &DISPLAY=DESC (19.06.08).
[3] Lamprontia, Phytomedicine 10 (2003) 300–308.
[4] http://www.wipo.int/pctdb/en/wo.jsp?wo=2006046159 (26.06.08).
[5] C. Plato, A.R. Glasgow Jr., Anal. Chem. 41 (1969) 330–336.
[6] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L.P. Leitão, M.V. Roux, L.A. Torres, Thermochim. Acta 331 (1999) 93–204.
[7] Aldrich, Handbook of Fine Chemicals and Laboratory Equipment, 2004–2005, Madrid, Spain.
[8] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, G. Pilcher, Rev. Port. Quím. 26 (1984) 163–172.
[9] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, G. Pilcher, J. Chem. Thermodyn. 16 (1984) 1149–1155.
[10] H.A. Skinner, A. Snelson, Trans. Faraday Soc. 56 (1960) 1776–1783.
[11] L.M.N.B.F. Santos, M.T. Silva, B. Schröder, L.J. Gomes, Therm. Anal. Cal. 89 (2007) 175–180.
[12] J. Coops, R.S. Jessup, K. Van Nes, in: F.D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience, New York, 1956 (Chapter 3).
[13] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nutall, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982).
[14] E.N. Washburn, J. Res. Nat. Bur. Stand. (US) 10 (1933) 525–558.
[15] W.N. Hubbard, D.W. Scott, G. Waddington, in: F.D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience, New York, 1956 (Chapter 5).
[16] M.E. Wieser, Pure Appl. Chem. 78 (2006) 2051–2066.
[17] F.A. Adedeji, D.L.S. Brown, J.A. Connor, M. Leung, M.I. Paz-Andrade, H.A. Skinner, J. Organomet. Chem. 97 (1975) 221–228.
[18] J.S. Chickos, W.E. Acree, J. Phys. Chem. Ref. Data 31 (2002) 537–698.
[19] J.S. Chickos, W.E. Acree Jr., J. Phys. Chem. Ref. Data 32 (2003) 519–878.
[20] D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
[21] T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1998) 785–789.
[22] P.C. Hariharan, J.A. Pople, Chem. Phys. Lett. 16 (1972) 217–219;
M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 80 (1982) 3654–3665.
[23] P.A. Scott, L. Radom, J. Chem. Phys. 100 (1996) 16502–16513.
[24] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213–222;
M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1884) 3265–3269.
[25] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007–1023;
D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 98 (1993) 1358–1371;
D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 100 (1994) 2975–2988;
A.K. Wilson, D.E. Woon, K.A. Peterson, T.H. Dunning Jr., J. Chem. Phys. 110 (1999) 7667–7676.
[26] B.J. Lynch, D.G. Truhlar, J. Phys. Chem. A 107 (2003) 3898–3906.
[27] Y. Zhao, B.J. Lynch, D.G. Truhlar, Phys. Chem. Chem. Phys. 7 (2005) 43–52.
[28] 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.
[29] The DFT module within GAMESS-UK was developed by Dr. P. Young under the auspices of EPSRC's Collaborative Computational Project No. 1 (CCP1) (1995–1997).
[30] Y. Zhao, D.G. Truhlar, MLGAUSS-Version 2.0, University of Minnesota, Minneapolis, 2004.
[31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota. R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.Q. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian Inc., Wallingford, CT, 2004.
[32] F.D. Rossini, in: F.D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience, New York, 1956 (Chapter 14).

[33] CODATA, J. Chem. Thermodyn. 10 (1978) 903–906.
[34] J.B. Pedley, Thermochemical Data and Structures of Organic Compounds, TRC Data Series, College Station, Texas, vol. 1, 1994.
[35] S. Verevkin, Thermochim. Acta 310 (1998) 229–235.
[36] M.A.R. Matos, C.C.S. Sousa, V.M.F. Morais, J. Chem. Thermodyn. (2008), doi:10.1016/j.jct.2008.06.019.
[37] M.A.R. Matos, C.C.S. Sousa, V.M.F. Morais, J. Phys. Chem. A 112 (2008) 7961–7968.
[38] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899–926.
[39] J.P. Foster, F. Weinhold, J. Am. Chem. Soc. 102 (1980) 7211–7218.
[40] A.E. Reed, F. Weinhold, J. Chem. Phys. 78 (1983) 4066–4073.
[41] E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, F. Weinhold, NBO 5.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2001.

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