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Thermochemistry and Gas-Phase Ion Energetics of 2-Hydroxy-4-methoxy-benzophenone (Oxybenzone)

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We have investigated the thermochemistry and ion energetics of the oxybenzone (2-hydroxy-4-methoxy-benzophenone, $C_{14}H_{12}O_3$, **1**H) molecule. The following parameters have been determined for this species: gas-phase enthalpy for the of neutral molecule at 298.15K, ($\Delta_f H_m^0(g) = -303.5 \pm 5.1$ kJ·mol^{-1}), the intrinsic (gas-phase) acidity (GA(**1**H) = 1402.1 ± 8.4 kJ·mol^{-1}), enthalpy of formation for the oxybenzone anion ($\Delta_f H_m^0(\mathbf{1}^-,g) = -402.3 \pm 9.8$ kJ·mol^{-1}). We also have obtained the enthalpy of formation of, 4-hydroxy-4′-methoxybenzophenone ($\Delta_f H_m^0(g) = -275.4 \pm 10$ kJ·mol^{-1}) and 3-methoxyphenol anion ($\Delta_f H_m^0(C_7H_7O_2^-,g) = -317.7 \pm 8.7$ kJ·mol^{-1}). A reliable experimental estimation of enthalpy related to intramolecular hydrogen bonding in oxybenzone has also been obtained (30.1 ± 6.3 kJ·mol^{-1}) and compared with our theoretical calculations at the B3LYP/6-311++G** level of theory, by means of an isodesmic reaction scheme. In addition, heat capacities, temperature, and enthalpy of fusion have been determined for this molecule by differential scanning calorimetry.

1. Introduction

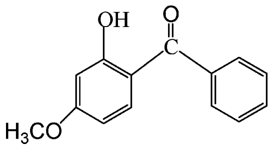
Some derivatives of benzophenone are important because of their physicochemical properties. Among them, their capability to efficiently absorb UV radiation over the 200−350 nm range is quite relevant. Indeed, this has led to the extensive use of compounds such as 2-hydroxy-4-methoxybenzophenone (oxybenzone, **1**H, $C_{14}H_{12}O_3$, Scheme 1) as sunscreens.

Interestingly, studies about shifts in their UV absorption spectra and solvent effects indicate that hydrogen bonding is a key interaction between sunscreen active ingredients and solvent.[1]

Although at this point there is some controversy about the side-effects of sunscreens[2,3] commercial products containing oxybenzone have so far proven effective in the long-term reduction of skin cancer and lesions such as actinic keratosis.

The purpose of this work was to address two areas: (i) Getting a quantitative estimate of the strength of chelation in neutral **1**H. This information was obtained through the determination of the standard enthalpy of formation of gaseous **1**H, **1**H(g). This, in turn, required the determination of the standard enthalpy of formation of crystalline **1**H by means of combustion calorimetry and its standard enthalpy of sublimation, using the Knudsen effusion technique. Also, thermophysical properties of **1**H(s) were determined by means of differential scanning calorimetry (DSC). (ii) Getting the intrinsic (gas phase) acidity of **1**H. It is related to chelation and, furthermore, allows one to get information on the structure and properties of the anion $\mathbf{1}^-$(g). This study was carried out by means of Fourier transform ion cyclotron resonance spectroscopy (FT-ICR). All these experimental studies were supplemented by a computational treatment. It is interesting that, notwithstanding the interest of **1**H, all this basic information has so far been unavailable.

SCHEME 1



The present work is part of a systematic investigation of the thermochemistry and thermophysics of large conjugated organic molecules of biological, medicinal, and industrial interest.[4]

2. Experimental Section

2.1. Purity and Phase Transition Control: DSC Measurements. The sample used in this work was obtained from Avocado (nominal mass fraction, 0.99). It was carefully dried under vacuum at 30 °C and used without further purification. This sample was investigated by differential scanning calorimeter (DSC) over the 260−336.7 K (melting point) range, with no phase transition in the solid state being observed. The heat capacities, temperature, and enthalpy of fusion were also experimentally determined by DSC.[5] Full details are given in the Supporting Information (S1).

2.2. Combustion Calorimetry. The combustion experiments were performed in an isoperibol static bomb calorimeter, described in detail elsewhere.[6−8] The energy equivalent of the calorimeter (ϵ calor) was determined from the combustion of benzoic acid (NIST standard reference sample 39j), its massic energy of combustion being −26434 ± 3 J·g^{-1}, under certificate conditions. From 10 calibration experiments, we obtained ϵ(calor) = (14262.6 ± 2.5) J·K^{-1}, where the uncertainty quoted is the standard deviation of the mean value. Complementary details are given in the Supporting Information (S2).

2.3. Knudsen-Effusion Method. The vapor pressures of the oxybenzone were measured as a function of temperature with the mass-loss Knudsen effusion method, according to the

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procedure previously described.[9−12] Full details are given in the Supporting Information (S3).

2.4. Ion Energetics: FT-ICR[13−16] Proton Exchange Study. Gas-phase experiments were carried out in a modified Bruker CMS-47 FT-ICR mass spectrometer[17] equipped with a 4.7 T superconducting magnet and controlled by an IonSpec Omega Data Station (IonSpec Corp., Irvine, CA). This instrument has been used in some recent studies.[18−20]

Determination of Gas-Phase Acidities. Mixtures of oxybenzone **1**H and a reference acid ($A_{ref}H$) of well-known gas-phase acidity were introduced into the high-vacuum chamber. Typical partial pressures were in the range of 2×10^{-8} to 1×10^{-7} mbar. The average temperature of the cell was about 331 K. *Isoamyl* nitrite (*iso*-$C_5H_{11}NO_2$) containing approximately 20% of methanol was also added. The resonant capture of electrons provided a mixture of *iso*-$C_5H_{10}O^-$ and CH_3O^-, which were protonated by oxybenzone and $A_{ref}H$ to yield exclusively a mixture of oxybenzone anion, $\mathbf{1}^-$, and A^-_{ref}. Reversible proton transfer, reaction 1, was monitored for 10−30 s until a state of equilibrium was reached. Double resonance experiments fully confirmed the reversibility of reaction (1)

$$\mathbf{1}H(g) + A^-_{ref}(g) \rightleftarrows A_{ref}H(g) + \mathbf{1}^-(g) \qquad K_p, \Delta_r G°_m \qquad (1)$$

A Bayard-Alpert ion gauge was used to measure the pressures of the neutral reactants with appropriate correction factors.[21] By definition, the gas phase acidity of oxybenzone, GA(**1**H), is the standard Gibbs energy change for reaction (2), $\Delta_r G°_m(2)$.

$$\mathbf{1}H(g) \rightleftarrows \mathbf{1}^-(g) + H^+ \qquad \Delta_r G°_m(2) = GA(\mathbf{1}H) \qquad (2)$$

Its value can be determined from GA($A_{ref}H$) and K_p, through eq 3

$$GA(\mathbf{1}H) = GA(A_{ref}H) - RT \ln K_p \qquad (3)$$

3. Computational Details

The quantum chemical calculations were carried out using the Gaussian 03 package.[22] The geometries of the compounds under investigation as well as those of the reference systems used in the isodesmic reaction considered were optimized by using density functional theory (DFT), with the Becke 3-parameter and Lee−Yang−Parr (B3LYP) functional[23,24] and the 6-311++G** basis set without symmetry restrictions. Harmonic vibrational frequencies were also calculated at the same level without scaling.

The level of theory employed in the present work is expected to provide reasonable values of reaction energetics.[25−27]

The structure for the transition states (TSs) among conformers were optimized using the methodology QST2,[22] where the transition structure connects the known structures of reactants and products. The TSs were characterized by one imaginary frequency.

The intrinsic gas phase acidity of oxybenzone was also calculated at the B3LYP/6-311+G(3df,2p) level, which is known[28] to reproduce very well the experimental results.

4. Results and Discussion

4.1. Thermophysical Properties. The temperature and enthalpy of fusion were determined by DSC technique as T_{fus}= (336.7 ± 0.5) K and $\Delta_{fus}H^0_m$ = (21.77 m ± 0.07) kJ·mol^{-1}, respectively. The uncertainties are expressed as the standard deviation of the mean experimental values.

TABLE 1: Experimental Determination of Standard Molar Enthalpies of Sublimation, Formation (in the Crystalline and Gaseous States at T = 298.15 K and p^0= 101.325 kPa), and Gas-Phase Acidity of 1H

$\Delta_f H^0_m$(cr)/ kJ·mol^{-1}	$\Delta_{sub}H^0_m$/ kJ·mol^{-1}	$\Delta_f H^0_m$(g)/ kJ·mol^{-1}	*GA*(**1**H)/ kJ·mol^{-1}
−414.2 ± 4.5	110.7 ± 2.5	−303.5 ± 5.1	1402.1 ± 8.4

Molar heat capacities were measured from the temperature T = 268 K to near its melting point. The corresponding results are given in Table S1 of the Supporting Information. The least-squares fitting of the experimental data yields eq 4 for the molar heat capacity curve, as a function of the temperature, in the range from 268.15 to 320.15 K.

$$C^0_{p,m}(cr)(J\cdot mol^{-1}\cdot K^{-1}) = -0.0006\cdot T^2 + 0.5121\cdot T - 68.429 \; (R^2 = 0.9997) \qquad (4)$$

4.2. Combustion Calorimetry and Knudsen Effusion Technique. *Enthalpy of Formation of the Neutral Molecule.* The process involved in the combustion of **1**H is portrayed in reaction 5:

$$\mathbf{1}H(cr) + 3.5O_2(g) \rightarrow 14CO_2(g) + 6H_2O(l) \qquad (5)$$

Full details are presented in the Supporting Information (Table S2).

The standard molar enthalpies of combustion, $\Delta_c H^0_m$(cr), and formation, $\Delta_f H^0_m$(cr), in the crystalline state at temperature T = 298.15 K are (−6809.9 ± 4.1) and (−414.2 ± 4.5) kJ·mol^{-1}, respectively. Their uncertainties are twice the final overall standard deviation of the mean, and were estimated as outlined by Olofsson.[29] The values for the standard molar enthalpies of formation of H_2O(l) and CO_2(g) at T = 298.15 K are (−285.830 ± 0.042) kJ·mol^{-1} and (−393.51 ± 0.13) kJ·mol^{-1}, respectively, taken from CODATA.[30]

The results from the Knudsen effusion experiments are summarized in Table S3 of the Supporting Information. These experimental results were fitted to the Clausius−Clapeyron eq 6,

$$\ln(p/Pa) = A - B\cdot(T/K^{-1}) \qquad (6)$$

The parameters A and B in this equation are (36.9 ± 1.0) and (−13108 ± 301), respectively. The molar enthalpy of sublimation, corresponding to the mean temperature [T_m] = 313.48 K of its experimental range, $\Delta_{sub}H^0_m[T_m]$ = (109.0 ± 2.5) kJ·mol^{-1}, has been calculated from the corresponding value of the parameter B. The uncertainty assigned to the value of $\Delta_{sub}H^0_m$ is based on the error attributed to the slope B.

The molar enthalpy of sublimation at 298.15 K was computed using eq 7:

$$\Delta_{sub}H^0_m(T = 298.15\text{ K}) = \Delta_{sub}H^0_m(T_m) + \int_{T_m}^{298.15} [C^0_{p,m}(g) - C^0_{p,m}(cr)]dT \qquad (7)$$

where $C^0_{p,m}(g) = -22.3 + 0.780(T/K) - 5 \times 10^{-4}(T/K)^2$ has been calculated by using the group contribution scheme, following the procedure reported by Rihani and Doraiswami,[31] and $C^0_{p,m}(cr)$ was taken from the experimental results obtained from eq 4.

The standard molar enthalpies of sublimation and formation of oxybenzone, in crystalline and gaseous states, at T = 298.15 K are given in Table 1.

TABLE 2: Computational Results (Total Energies at 0 K, Enthalpies and Free Energy at 298.15 K, and OH Stretching Vibrational Numbers σ) at the B3LYP/6-311++G Level for Conformers of Oxybenzone, Its Isomer 4-Hydroxy-4′-methoxy Benzophenone, Transition States (TS), and Reference Compounds**

compounds		$E_0{}^a$	$G_{298}{}^a$	$H_{298}{}^a$	σ (OH)^b
oxybenzone	$\mathbf{1}H_a$	−766.373192	−766.414951	−766.358144	3266.3
	$(\mathbf{1}H_b)^c$	(−766.371796)	(−766.413726)	(−766.356675)	(3320.2)
	$\mathbf{TS}_{\mathbf{1}Ha-\mathbf{1}Hb}$	−766.366180	−766.407315	−766.351680	3322.7
	$\mathbf{TS}_{\mathbf{1}Ha-\mathbf{2_a}}$	−766.355004	−766.396650	−766.339996	3827.1
	$\mathbf{2_a}$	−766.360203	−766.402395	−766.344738	3759.5
	$(\mathbf{2_b})^c$	(−766.359578)	(−766.401943)	(−766.344049)	(3769.1)
	$\mathbf{3_a}$	−766.356060	−766.398833	−766.340339	3836.4
	$(\mathbf{3_b})^c$	(−766.356966)	(−766.399648)	(−766.341263)	(3832.1)
	$\mathbf{4_a}$	−766.354191	−766.397039	−766.338476	3835.9
	$(\mathbf{4_b})^c$	(−766.354855)	(−766.397677)	(−766.339166)	(3833.1)
4-hydroxy-4′-methoxy benzophenone	$\mathbf{I_a}$	−766.362573	−766.405155	−766.346992	3830.0
	$(\mathbf{I_b})^c$	(−766.362528)	(−766.405156)	(−766.346942)	(3830.0)
	$\mathbf{II_a}$	−766.362572	−766.405151	−766.346991	3830.0
	$(\mathbf{II_b})^c$	(−766.362526)	(−766.405153)	(−766.346941)	(3829.1)
	$\mathbf{III_a}$	−766.362361	−766.404931	−766.346790	3830.0
	$(\mathbf{III_b})^c$	(−766.362243)	(−766.404854)	(−766.346668)	(3830.7)
	$\mathbf{TS_{Ia-IIa}}$	−766.357557	−766.399205	−766.342596	3835.0
	$\mathbf{TS_{Ia-Ib}}$	−766.357446	−766.399388	−766.342440	3828.6
	$\mathbf{TS_{Ia-IIIa}}$	−766.356801	−766.399182	−766.341589	3825.4
benzene		−232.211107	−232.236225	−232.205764	
benzophenone (**Bz$_2$CO**)		−576.591416	−576.629102	−576.579684	
3-methoxyphenol (**3-MeOPhOH**) conformers	−421.979552	−422.012272	−421.970370	3836.6	
		−421.979247	−422.011937	−421.970097	3835.6
		−421.979146	−422.011878	−421.969955	3840.1
		−421.978378	−422.011123	−421.969193	3840.0

^{a} All values in units of Hartree. ^{b} Values in cm^{-1}. ^{c} Values in the bracket correspond to the rotamers of the methoxy group.

4.3 The Experimental Gas-Phase Acidity of Oxybenzone. In each case, the K_p values (defined in reaction 3) were taken as the average of six different experiments involving different ratios of the pressures of the neutral acids. Experiment results are summarized in Table S4 of the Supporting Information. The estimated uncertainties, 1.9 kJ·mol^{-1}, is twice the standard deviation of the average. However, although this precision seems satisfactory, the accuracy of the GA($A_{ref}H$) values is given as 8.4 kJ·mol^{-1}, in accordance with the recommendations of NIST[32]. To summarize: GA(**1**H) = 1402.1 ± 8.4 kJ·mol^{-1} (Table 1).

4.4. Structures, Hydrogen-Bond and Thermochemical Properties of Oxybenzone Molecule. We present in Table 2 the computed energies for the relevant stable conformations of this compound. The notation $\mathbf{X_b}$ corresponds to the rotation of the methoxy-substituted moiety of $\mathbf{X_a}$ around the C_6-O_{16} bond.

Structures **1**H$_a$ and **1**H$_b$ are chelated, while **2**, **3**, and **4** are not. Figure 1 shows the various conformers for the latter species. The dihedral angle $\omega = D(O_1-C_2-C_3-C_4)$, (or angle $\phi = D(O_1-C_2-C_9-C_{10})$) is formed by the plane containing the substituted (or unsubstituted) benzene ring and the plane of the rest of the molecule (See Figure 1a).

In terms of standard Gibbs energies, conformers **1**H$_a$ and **1**H$_b$ differ by 3.2 kJ·mol^{-1}, the latter being less stable. The dimensionless equilibrium constant K_8 pertaining to equilibrium 8 thus amounts to 3.7.

Furthermore, the change in standard Gibbs energy pertaining to process 9, that is, the activation barrier for reaction 8, amounts to 20.1 kJ·mol^{-1}:

$$\mathbf{1}H_a \rightleftarrows \mathbf{1}H_b \qquad K_8 \tag{8}$$

$$\mathbf{1}H_a \rightleftarrows \mathbf{TS}_{\mathbf{1}Ha-\mathbf{1}Hb} \tag{9}$$

It follows that, at ca. 298.15 K, a sample of gaseous oxybenzone is an equilibrating mixture of approximately 21.5 and 78.5% of **1**H$_b$ and **1**H$_a$, respectively.

Rotation of the phenolic moiety of **1**H$_a$ around the C3−C2-(O) bond leads to structure $\mathbf{2_a}$ in which the chelation [OH···O(C)] and also the interaction between the OH group and the unsubstituted phenyl moiety are absent. The computed standard Gibbs energy changes for reactions 10 and 11 are 33.0 and 48.1 kJ·mol^{-1}, respectively, and close values are found for similar processes involving species **1**H$_b$ and **2**$_b$.

$$\mathbf{1}H_a \rightleftarrows \mathbf{2_a} \tag{10}$$

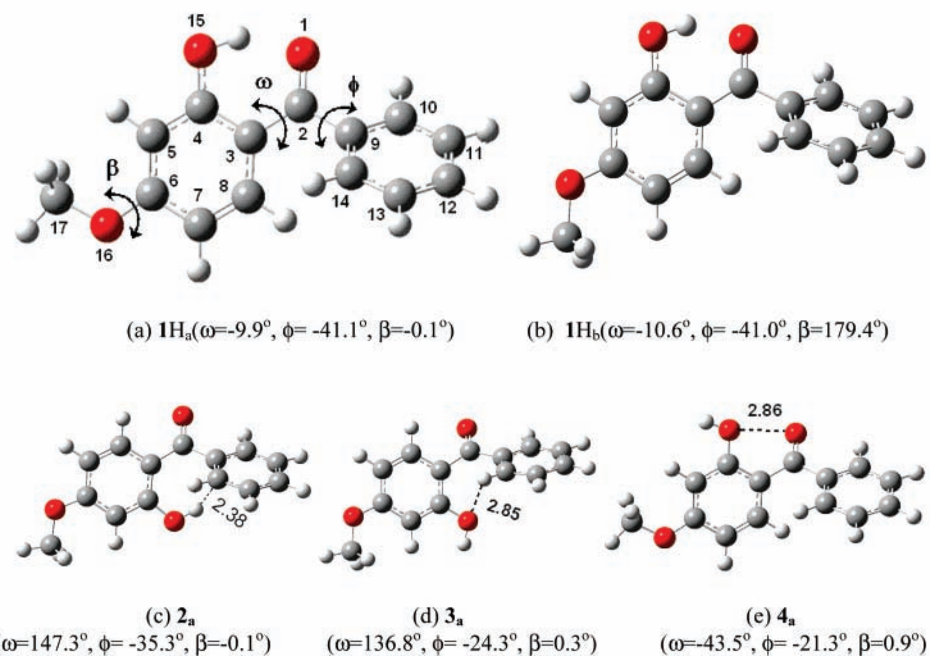
$$\mathbf{1}H_a \rightleftarrows \mathbf{TS}_{\mathbf{1}Ha-\mathbf{2}a} \tag{11}$$

These results indicate that, under normal conditions, process 10 is quite unfavorable (e.g., the equilibrium molar fraction of $\mathbf{2_a}$ can be estimated at ca. 1.7 × 10^{-6}) and rather slow.

Furthermore, rotation of the hydroxyl group in $\mathbf{2_a}$ around the C4−OH bond leads to structure $\mathbf{3_a}$. Rotation of the same group in structure **1**H$_a$ leads to structure $\mathbf{4_a}$, wherein chelation is also destroyed. Inspection of the data reported in Table 3 indicates that their stabilities (as measured in terms of enthalpies or Gibbs energies) are even smaller than that of $\mathbf{2_a}$, and therefore these conformers are not quantitatively relevant in the case of a gaseous sample of oxybenzone.

Rotation of the unsubstituted benzene moiety of **1**H$_a$ ($\omega = -10°$, $\phi = -41°$) around the C9−C2(O) bond leads to the formation of its enantiomer **1′**H$_a$ ($\omega = +10°$, $\phi = +41°$). This happens for all $\mathbf{X_a}$ and $\mathbf{X_b}$ conformers (also including anionic species).

In general, our computational results for the structure of **1**H were in good agreement with the available experimental data (obtained from X-ray diffraction, XRD, results[33]), although some discrepancies relative to distance $d(H\cdots O_1)$, between the carbonyl oxygen O_1 and the hydrogen of OH group, were observed



(a) **1**H$_a$(ω=-9.9°, φ= -41.1°, β=-0.1°) (b) **1**H$_b$(ω=-10.6°, φ= -41.0°, β=179.4°)

(c) **2$_a$** (ω=147.3°, φ= -35.3°, β=-0.1°) (d) **3$_a$** (ω=136.8°, φ= -24.3°, β=0.3°) (e) **4$_a$** (ω=-43.5°, φ= -21.3°, β=0.9°)

Figure 1. Molecular geometry for stable conformers of oxybenzone optimized at the B3LYP/6-311++G** level.

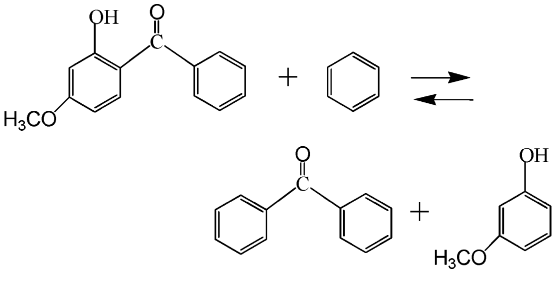
TABLE 3: Experimental and Calculated Geometrical Parameters of Oxybenzone

	B3LYP/6-311++G** level		
	1H$_a$	**1**H$_b$	experimental[a]
d(H···O$_1$)[b]	1.661	1.679	1.575
d(H−O$_{15}$)[c]	0.992	0.989	1.038
d(O$_1$−O$_{15}$)	2.555	2.568	2.551
$\omega = D(O_1{-}C_2{-}C_3{-}C_4)$[d]	−9.9	−10.6	−9.7
$\phi = D(O_1{-}C_2{-}C_9{-}C_{10})$[e]	−41.2	−41.1	−41.3
$D(C_7{-}C_4{-}C_{10}{-}C_{13})$[f]	−48.8	−49.3	−47.7
$\beta = D(C_5{-}C_6{-}O_{16}{-}C_{17})$[g]	−0.1	179.4	0.9

[a] Taken from ref 33. [b] Distance (in Å) between the carbonyl oxygen O$_1$ and the hydrogen of the OH group. [c] Distance (in Å) between the hydrogen and oxygen of the OH group. [d] Dihedral angles (in degrees) formed by planes containing single bond C(3)−CO. [e] Dihedral angles formed by planes containing single bond C(9)−CO. [f] Dihedral angles formed by planes containing aromatic rings. [g] Dihedral angles formed by planes containing single bond C(6)−OCH$_3$.

(Table 3). These small discrepancies can be attributed to the fact that the experiment is performed in crystal, while the calculations refer to the gas phase.

Isodesmic reaction schemes are widely used in predicting molecular stability.[27,34−40] Here, reaction 12 was constructed. It is associated with intramolecular H-bond breaking/forming in oxybenzone. Otherwise, both the number and kind of the other bonds in the process are the same.

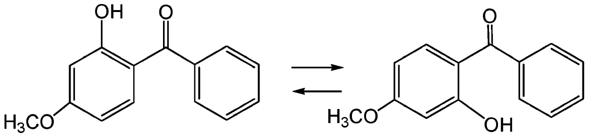


(12)

The well-known experimental $\Delta_f H^0_m$(g) values of benzene (82.93 ± 0.50 kJ·mol^{-1}),[32] benzophenone, **Bz$_2$CO** (49.9 ± 3.0 kJ·mol^{-1}),[32] and 3-methoxyphenol, **3-MeOPhOH** (−240.4 ± 2.1 kJ·mol^{-1})[41] were combined with the $\Delta_f H^0_m$(g) value of oxybenzone determined in this work. The enthalpy associated with the O−H···O$_1$ interaction in oxybenzone was estimated using purely experimental data as the enthalpy of reaction 12, $\Delta_r H^0(12) = 30.1 \pm 6.3$ kJ·mol^{-1}. The endothermicity of this reaction indicates that the presence of O−H···O$_1$ interaction in oxybenzone has a stabilizing effect. Our experimental quantification of intramolecular H-bonding in oxybenzone agrees, within the experimental uncertainties, with the following computational results:

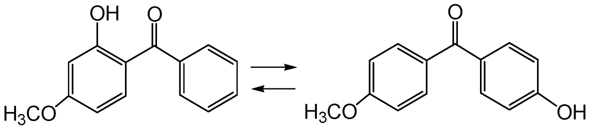
(1) The enthalpy, obtained by taking into account the conformers contributions, with reaction 12 is $\Delta_r H^0(12)_{\mathrm{comput}} = 36.8$ kJ·mol^{-1}.

(2) In the homodesmotic reaction 13, the most stable chelated **1**H conformers are compared to those less stable (nonchelated) **2**, **3**, and **4**, where the intramolecular H-bond is absent. We find that the enthalpy of this reaction is $\Delta_r H^0_m(13) = 35.6$ kJ·mol^{-1}.



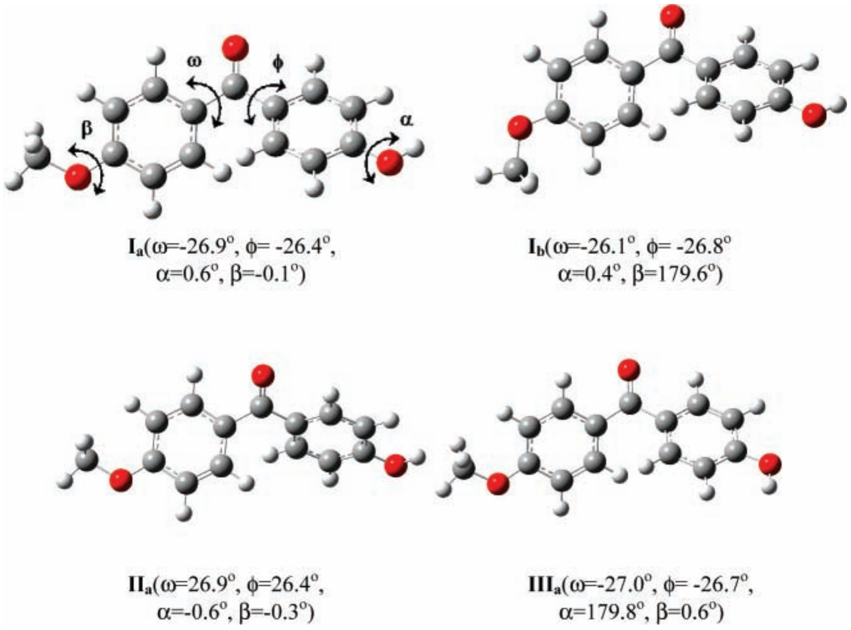
(13)

(3) In the homodesmotic reaction 14, oxybenzone **1**H is compared with its isomer 4-hydroxy-4′-methoxybenzophenone. The corresponding enthalpy of reaction is $\Delta_r H^0_m(14) = 28.7$ kJ·mol^{-1}. This value takes into account the contribution of several conformers of these species, where the interaction H-bonding is absent, and all of them exhibit practically the same enthalpy of formation (differences of less than 1 kJ·mol^{-1}).



(14)

Figure 2 shows some of these conformers, obtained from **I$_a$** by rotation of the rings (i.e., **I$_a$**−**II$_a$**), methoxy (i.e., **I$_a$**−**I$_b$**), or



$\mathbf{I_a}$(ω=-26.9°, ϕ= -26.4°, α=0.6°, β=-0.1°)

$\mathbf{I_b}$(ω=-26.1°, ϕ= -26.8° α=0.4°, β=179.6°)

$\mathbf{II_a}$(ω=26.9°, ϕ=26.4°, α=-0.6°, β=-0.3°)

$\mathbf{III_a}$(ω=-27.0°, ϕ= -26.7°, α=179.8°, β=0.6°)

Figure 2. Molecular geometry for some stable conformers of 4-hydroxy-4′-methoxybenzophenone optimized at the B3LYP/6-311++G** level.

OH (i.e., $\mathbf{I_a}-\mathbf{III_a}$) groups, with activation barriers (in terms of standard Gibbs energies) of 15.6, 15.1, and 15.7 kJ·mol^{-1}, respectively. We should mention that, by taking into account the value of $\Delta_r H_m^0(14)$ we can obtain the enthalpy of formation in the gas phase of 4-hydroxy-4′-methoxybenzophenone, $\Delta_f H_m^0(g) = -275.4$ kJ·mol^{-1} with an estimated uncertainty of ± 10.0 kJ·mol^{-1}.

(4) The wave-numbers σ(OH)[42] for the OH stretching vibration, have long been considered to be properties extremely sensitive to hydrogen-bond interactions.[43] Here, the calculated σ(OH) values for oxybenzone **1**H$_a$ and **1**H$_b$ are 3266 and 3320 cm^{-1}, respectively, while σ(OH) for non-H-bonded structures such as **2**, **3**, **4**, **I**, **II**, and **III** are between 3759.5 and 3836.4 cm^{-1} (Table 3). Thus, the average red-shift of the OH stretching vibration in normal (chelated) **1**H relative to a hypothetical unchelated isomer, $\Delta\sigma$(OH), amounts to ca. 500 cm^{-1}, that is, a 14% effect. Experimental data on the gas-phase IR spectra of monomeric unsubstituted phenol and 2-hydroxybenzophenone are available.[44] The $\Delta\sigma$(OH) for these two species amounts to 475 cm^{-1}, a value quite comparable to that indicated above for **1**H. Furthermore, solution (CCl$_4$) data for the interaction between phenols and acetophenone or benzophenone are also available.[45] In the absence of information for the 3-methoxyphenol/benzophenone system, we take the 4-bromophenol/acetophenone couple as a reasonable model. The standard enthalpy change for the formation of the 1:1 complex amounts to 16.4 kJ/mol (acetophenone is a better H-bond acceptor than benzophenone). For the system 4-bromophenol/benzophenone, the $\Delta\sigma$(OH) value associated with the interaction between the OH group and the "lone pairs" of the carbonyl groups amounts to 218 cm^{-1}.[45] There is a significant difference between these systems and **1**H.[43] The last result, in combination with geometric data, such as d(H···O$_1$) or O$_{15}$−H···O$_1$ angle (147.7° and 147.3° for **1**H$_a$ and **1**H$_b$, respectively), and energetic results described above allow us to classify the hydrogen bond in oxybenzone **1**H as a "moderate"[46] or "conventional-strong"[47] bond, which has an electrostatic character and belongs to the most common kind of H-bond in both chemistry and nature. The values for σ(OH) and d(O$_1$−O$_{15}$) of **1**H (Tables 2 and 3) are well within the range of the linear correlation between the O−H stretching wavenumber and the O···O distance for chelated compounds reported in classical studies.[48,49] Neutron diffraction studies[50] allowed the accurate comparison of d(O−H) and d(O···O) values for a wide variety of hydrogen-bonded systems. The experimental and calculated values for **1**H are quite consistent with the empirical relationship between these values obtained in these studies. In this respect, d(O$_1$···O$_{15}$) is rather short and the hydrogen bond significantly bent (O$_{15}$−H···O$_1$ angle of ca. 147.5°).

4.5. Intrinsic (Gas Phase) Acidity of 1H: Structural and Energetic Features of $\mathbf{1^-}$ ($\mathbf{C_{14}H_{11}O_3^-}$). The possible conformers of $\mathbf{1^-}$. The structures of the various stable anions formed by OH-deprotonation of **1**H are presented in Figure 3. The computed energies for these species are summarized in Table 4. The geometry changes upon deprotonation of **1**H are significant. Let us comment on the most important ones: (a) The conformers $\mathbf{1^-_a}$ ($\mathbf{1^-_b}$) and $\mathbf{2^-_a}$ ($\mathbf{2^-_b}$) resemble the neutral rotamers $\mathbf{2_a}$ ($\mathbf{2_b}$) and **1**H$_a$ (**1**H$_b$), respectively. (b) The bond length (O$_1$−C$_2$) (≈ 1.24 Å) of the C=O group remains practically unchanged, while the bond length (O$_{15}$−C$_6$) significantly shortens (by ∼0.1 Å) upon deprotonation.

In terms of standard Gibbs energies, conformers $\mathbf{1^-_a}$ and $\mathbf{1^-_b}$ differ by 6.7 kJ·mol^{-1}, the former being more stable. The dimensionless equilibrium constant K_{15} pertaining to equilibrium 15 thus amounts to 15.1. The activation barrier for this process (reaction 16) is 13.4 kJ·mol^{-1}.

$$\mathbf{1^-_a} \rightleftarrows \mathbf{1^-_b} \qquad K_{15} \tag{15}$$

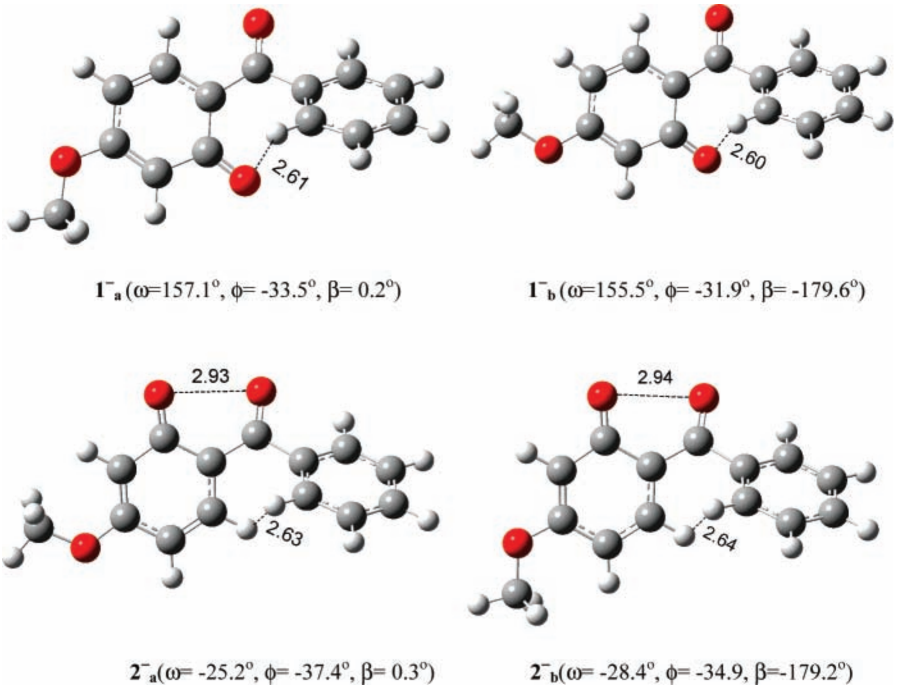
$$\mathbf{1^-_a} \rightleftarrows \mathbf{TS^-_{1a-1b}} \tag{16}$$

It follows that, at ca. 298.15 K, $\mathbf{1^-}$ is expected to be an equilibrating mixture of $\mathbf{1^-_a}$ (93.8%) and $\mathbf{1^-_b}$ (6.2%).

Rotation of the methoxy-substituted moiety of $\mathbf{1^-_a}$ around the C3−C2(O) bond leads to structure $\mathbf{2^-_a}$. The computed standard Gibbs energy changes for reactions 17 and 18 are 20.3 and 35.7 kJ·mol^{-1}, respectively.

$$\mathbf{1^-_a} \rightleftarrows \mathbf{2^-_a} \tag{17}$$

$$\mathbf{1^-_a} \rightleftarrows \mathbf{TS^-_{1a-2a}} \tag{18}$$



1^-_a (ω=157.1°, ϕ= -33.5°, β= 0.2°) 1^-_b (ω=155.5°, ϕ= -31.9°, β= -179.6°)

2^-_a(ω= -25.2°, ϕ= -37.4°, β= 0.3°) 2^-_b(ω= -28.4°, ϕ= -34.9, β=-179.2°)

Figure 3. B3LYP/6-311++G** optimized geometries for stable conformers of oxybenzone anion ($C_{14}H_{11}O_3^-$).

TABLE 4: Computational Results (Total Energies at 0 K, Enthalpies and Free Energy at 298.15 K) at the B3LYP Level with (a) 6-311++G Base for Oxybenzone Anion Conformers and Their Transition States (TS) and Also for 3-Methoxyphenol Anion Conformers, and (b) 6-311+G(3df,2p) Base for the Most Stable Conformers of Oxybenzone Neutral ($C_{14}H_{12}O_3$) and Anion ($C_{14}H_{11}O_3^-$)**

species		E_0[a]	G_{298}[a]	H_{298}[a]
oxybenzone	**1**H$_a$	(−766.427786)	(−766.469545)	(−766.412738)
($C_{14}H_{12}O_3$)	**1**H$_b$	(−766.426390)	(−766.468320)	(−766.411269)
oxybenzone anion	$\mathbf{1^-_a}$	−765.830913	−765.873503	−765.815567
($C_{14}H_{11}O_3^-$)		(−765.883850)	(−765.926440)	(−765.868504)
	$\mathbf{1^-_b}$	−765.827969	−766.870939	−765.812514
		(−765.881134)	(−765.924104)	(−765.865679)
	$\mathbf{TS^-_{1a--1b}}$	−765.826621	−765.868405	−765.811875
	$\mathbf{2^-_a}$	−765.822844	−765.865780	−765.807406
	$\mathbf{TS^-_{2a-1a}}$	−765.818044	−765.859912	−765.803308
	$\mathbf{2^-_b}$	−765.819752	−765.863358	−765.804156
3-methoxyphenol		−421.430304	−421.462975	−421.421430
anion ($C_7H_7O_2^-$)		−421.428867	−421.461960	−421.419824

[a] All values in units of Hartree. Values in the bracket correspond to the base 6-311+G(3df,2p).

These results indicate that process 17 is quite unfavorable and rather slow. The equilibrium molar fraction of $\mathbf{2^-_a}$ can be estimated at ca. 2.8 × 10^{-4}. Furthermore, rotation of the methoxy group in $\mathbf{2^-_a}$ leads to structure $\mathbf{2^-_b}$, which is 6.4 kJ·mol^{-1} less stable. Thus, conformers $\mathbf{2}^-$ do not seem to significantly contribute to the total population of oxybenzone anion.

The experimental values of GA(**1**H) and $\Delta_f H^0_m$(**1**H) determined in this work, together with $\Delta_f H^0_m(H^+)$[51] lead to a purely experimental value of $\Delta_f H^0_m(\mathbf{1}^-)$ provided the experimental $\Delta_r S^0_m(2)$ is known. The standard entropy change for reaction 2 is given by eq 19:

$$\Delta_r S^0_m(2) = S^0_m(\mathbf{1}^-) + S^0_m(H^+) - S^0_m(\mathbf{1}H) \qquad (19)$$

$S^0_m(H^+)$ is known (108.95 J mol^{-1} K^{-1}),[51] but the difference $S^0_m(\mathbf{1}^-) - S^0_m(\mathbf{1}H)$ is not. In general, differences in S^0_m between neutral species and the ions derived therefrom by protonation or deprotonation are small and are often estimated by considering changes in symmetry numbers[32] only. Here, because of the presence of the chelation in **1**H and the major structural differences between **1**H and $\mathbf{1}^-$, we have used the computed values of S^0_m for these species taking into account the contributions from the various possible conformers. Full details are given in the Supporting Information (Table S5). We obtained $S^0_m(\mathbf{1}^-) - S^0_m(\mathbf{1}H) = 9.75$ J mol^{-1} K^{-1}, a rather small value. This leads to $\Delta_f H^0_m(\mathbf{1}^-) = -402.3 \pm 9.8$ kJ·mol^{-1}.

The experimental GA for 3-methoxyphenol (3-MeOPhOH) is available (1427.0 ± 8.4 kJ·mol^{-1}),[32] and so is its standard enthalpy of formation (see above). A treatment similar to that for $\mathbf{1}^-$ (full details given in Table S5) leads to a value of −317.7 ± 8.7 kJ·mol^{-1} for $\Delta_f H^0_m$(3-MeOPhO$^-$).

It is possible to envisage a process (reaction 20) similar to reaction 12 and involving the corresponding anionic species:

$$\mathbf{1}^-(g) + C_6H_6(g) \rightarrow C_6H_5COC_6H_5(g) + 3\text{-MeOPhO}^-(g) \qquad (20)$$

Using the experimentally based data reported above, we obtain $\Delta_r H^0_m(20) = 51.6$ kJ·mol^{-1}, a value nearly twice as large as $\Delta_r H^0_m(12)$. In the case of **1**H, chelation exerts an important stabilizing effect, and this keeps atoms O_1 and O_{15}

relatively close (see Table 3). In the case of the anionic forms, it is to be expected that a substantial part of the negative charge will spread over the entire ion, concentrating particularly on atoms O_1 and O_{15}. Indeed, this is confirmed by the NBO charge distribution calculations at the B3LYP/6-311+G(d,p) level. Natural charges on atoms O_1 and O_{15} respectively amount to -0.727 and -0.648 electronic units (the charge on O_{16} being -0.562). This charge-dispersal effect stabilizes the conformers of **1**$^-$. It is interesting that the modulus of the dipole moment for the two conformers of 3-MeOPhO$^-$ respectively amount to 6.35 and 8.38 D, while for conformers $\mathbf{1}^-_\mathbf{a}$ and $\mathbf{1}^-_\mathbf{b}$ they are equal to 2.88 and 2.84 D, respectively. This difference originates in the large separation between O_1 and O_{15} and the fact that the corresponding CO bond moments largely oppose each other.

The calculated theoretical gas phase acidity of oxybenzone, GA$_{\mathrm{comput}}$(**1**H), obtained by taking into account the contributions of the conformers (Tables 2 and 4) are 1395.0 and 1399.3 kJ·mol^{-1} for the 6-311++G** and 6-311+G(3df,2p) basis sets, respectively. Both values are close to the experimental datum, the latter being the closest.

An important point is that double resonance experiments show the extremely clean reversibility of reaction (1). It is fair to wonder how this can be, because collisions between **1**$^-$ and AH$_{\mathrm{ref}}$ can lead in principle to protonation on O_1 (the "wrong" oxygen) and O_{15} (the "right one", but too far away from O_1 to lead to the normal, chelated structure of **1**H). In fact, the species obtained by protonation at O_1 (full details are given in the Supporting Information Section S6) is a minimum on the potential energy surface (PES), but is significantly less stable than the species obtained by protonation on O_{15} (i.e., 70 kJ·mol^{-1} less stable than $\mathbf{2}_\mathbf{a}$, in terms of standard Gibbs energies). The latter, can lead to structures **2**, **3**, and **4**. All of them are significantly less stable than **1**H. Therefore, when GA(AH$_{\mathrm{ref}}$) approaches the "true" GA(**1**H), only protonation on O_{15} prevails, and the energy liberated in the formation of the collision complex (often near 100 kJ mol^{-1}) brings about the isomerization to the normal neutral form of **1**H.

5. Summary and Conclusions

The experimental and theoretical investigation of the thermochemistry, thermophysics, and ion energetic properties of the oxybenzone molecule was reported in this work. DSC, combustion calorimetry, Knudsen effusion, and FT-ICR experimental techniques, as well as quantum chemical calculations at the DFT level were employed. Relevant and consistent set thermochemical, ion energetics data and physical chemical properties have been derived for this molecule and its anion formed by deprotonation of the OH group. The experimental values of the enthalpy of formation of oxybenzone **1**H (-303.5 ± 5.1 kJ·mol^{-1}) has permitted us to obtain the following results: (i) a quantitative estimate of the strength of chelation in neutral **1**H (30.1 ± 6.3 kJ·mol^{-1}), (ii) the standard enthalpy of formation in gas phase of 4-hydroxy-4′-methoxybenzophenone, $\Delta_f H^0_m(g) = -275.4 \pm 10.0$ kJ·mol^{-1}, and (iii) the standard enthalpy of formation in gas phase of oxybenzone anion, $\Delta_f H^0_m(\mathbf{1}^-, g) = -402.3 \pm 9.8$ kJ·mol^{-1}. This last one also required the determination of the intrinsic (gas phase) acidity of **1**H, GA(**1**H) = 1402.1 ± 8.4 kJ·mol^{-1}. We also obtained the standard heat of formation in gas phase of 3-methoxyphenol anion, $\Delta_f H^0_m(\text{3-MeOPhO}^-, g) = -317.7 \pm 8.7$ kJ·mol^{-1}.

Finally, it is important to mention that our theoretical calculations provided interesting results that served to confirm the excellent consistency of our experimental measurements.

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Supporting Information Available: (S1) Experimental molar heat capacities and DSC measurements; (S2) combustion calorimetry; (S3) Knudsen-effusion method; (S4) experimental gas-phase acidity; (S6) species obtained by protonation at O_1; and (S5) total standard entropy, S^0_m. This material is available free of charge via the Internet at http://pubs.acs.org

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