

O–H Bond dissociation enthalpies in hydroxyphenols. A time-resolved photoacoustic calorimetry and quantum chemistry study†

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Received 7th November 2003, Accepted 24th February 2004
First published as an Advance Article on the web 16th March 2004

Time-resolved photoacoustic calorimetry (TR-PAC) was used to investigate the energetics of O–H bonds of phenol, catechol, pyrogallol, and phloroglucinol. Values of -27.1 ± 3.9 , -44.1 ± 4.4 and -1.6 ± 3.8 kJ mol⁻¹, respectively, were obtained for the solution-phase (acetonitrile) O–H bond dissociation enthalpies of the last three compounds relative to the O–H bond dissociation enthalpy in phenol, $\Delta DH_{\text{sln}}^{\circ}(\text{ArO–H}) = DH_{\text{sln}}^{\circ}(\text{ArO–H}) - DH_{\text{sln}}^{\circ}(\text{PhO–H})$. A value of 388.7 ± 3.7 kJ mol⁻¹ was determined for the PhO–H bond dissociation enthalpy in acetonitrile. Density functional theory (MPW1PW91/aug-cc-pVDZ) calculations and complete basis set (CBS-4M) calculations were carried out to analyse intramolecular hydrogen bonding and to predict gas-phase O–H bond dissociation enthalpies, $DH^{\circ}(\text{ArO–H})$. A microsolvation model, based on the DFT calculations, was used to study the differential solvation of the phenols and their radicals in acetonitrile and to bridge solution- and gas-phase data. The results strongly suggest that $\Delta DH_{\text{sln}}^{\circ}(\text{ArO–H}) \approx \Delta DH^{\circ}(\text{ArO–H})$. Hence, to calculate *absolute* gas-phase O–H bond dissociation enthalpies in substituted phenols from the corresponding solution-phase values, the solvation enthalpies of the substituted phenols and their radicals are *not* required.

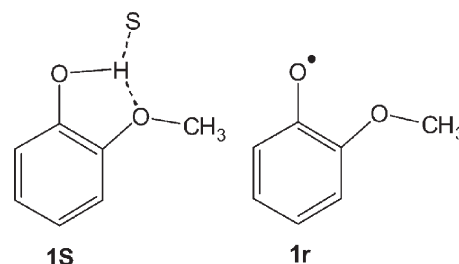
Introduction

The importance of phenolic compounds as chain-breaking antioxidants is well established.¹ One of the key features for this antioxidant performance is the *strength* of the O–H bond. For instance, if the phenolic compound acts as a hydrogen atom supplier to peroxy radicals, thus breaking the oxidation chain reaction,^{1b,e} then a weak O–H bond will make the phenolic hydrogen abstraction more favorable. The best chain-breaking antioxidants are therefore those compounds which have a low O–H bond dissociation enthalpy.

The thermochemical database on phenolic O–H bonds has grown considerably in the last decade,² allowing to estimate bond dissociation enthalpies for compounds that have not yet been subject to experimental or computational studies. Most of the available experimental data were obtained from solution studies, whereas the computational values typically refer to the “isolated” molecules (*i.e.* the bond dissociation enthalpies are tabulated for the molecules in the ideal gas phase). To make reliable comparisons between these sets of data one needs information on the solvation energetics of all the species involved, namely the parent phenol, the corresponding phenolic radical, and the hydrogen atom. While solvation effects have a small effect on the thermochemistry of many reactions, in other cases the solvent may play an important role in the reaction energetics. This happens, for example,

when the solvent has a strong hydrogen-donating and/or -accepting ability, because it may form strong intermolecular H-bonds with the reactants and/or the products.

Our knowledge of solvent effects on bond dissociation enthalpies (or solvation energetics of free radicals) is still scarce. Kanabus-Kaminska *et al.*³ have suggested that the solvation enthalpies of carbon-centered radicals (R[•]) and their parent molecules (RH) are similar both in polar and in non-polar solvents. This was confirmed by a recent study where the energetics of the C–H bonds in toluene, ethyl benzene, and cumene in solution were investigated.⁴ Wayner *et al.*⁵ argued that this conclusion does not hold for the phenoxy radical (PhO[•]) and phenol (PhOH) in hydrogen-acceptor solvents. More recently, de Heer *et al.*^{2g,6} extended these studies to phenolic systems where intra- and intermolecular H-bonds are involved. For instance, in the case of *ortho*-methoxyphenol in ethyl acetate (**1S**), the molecule is stabilized by an intramolecular H-bond and by an intermolecular H-bond with the solvent (S), whereas in the corresponding phenoxy radical (**1r**) no such bonds are possible. The enthalpies of those H-bonds were estimated as 18.4 kJ mol⁻¹ (intramolecular) and 11.7 kJ mol⁻¹ (intermolecular).^{2g}



† Electronic supplementary information (ESI) available: Table S1: Total energies calculated at the MPW1PW91/aug-cc-pVDZ and the CBS-4M levels. Data include zero point energies and thermal corrections to 298 K. See <http://www.rsc.org/suppdata/cp/b3/b314093h/>

A reason why the studies by de Heer *et al.* are important is that they show that if one uses the usual methods to predict the O–H bond dissociation enthalpy in a given solvent, based on the additivity of substituent effects or on Hammett plots,^{2a,g} an extra correction needs to be applied due to the intramolecular stabilization of **IS**. An interesting follow-up of these studies is investigating the energetics of molecules where the stabilization caused by an intramolecular H-bond may occur *both* in the parent phenol and in the corresponding phenoxy radical. Hydroxyphenols, which are models of many antioxidant compounds from the flavonoid family,¹ are particularly suited for that purpose. One of the aims of the present paper is therefore to report our findings concerning the thermochemistry of the O–H bonds in some hydroxyphenols, using time-resolved photoacoustic calorimetry (TR-PAC) and quantum chemistry calculations. A second goal of our studies is related to the commonly used method to bridge solution- and gas-phase O–H bond dissociation enthalpies.⁵ This method relies on the assumption that the difference between the solvation enthalpies of a phenolic compound and the related phenoxy radical is approximately equal to the enthalpy of the intermolecular H-bond involving the phenol compound and the hydrogen-acceptor solvent, which, of course, does not occur in the radical–solvent pair. Using quantum chemistry calculations and experimental data, we have tested this assumption and searched for better ways of estimating the *differential* solvation energetics of O–H homolysis reactions.

Experimental

Photoacoustic calorimetry

The photoacoustic calorimeter setup and the experimental technique have been described in detail.^{4,7–9} Briefly, argon-purged solutions in acetonitrile of *ca.* 0.4 M of di-*tert*-butyl peroxide and each hydroxyphenol (in the appropriate concentration; see Results and discussion) were flowed through a quartz flow cell (Hellma 174-QS). As pyrogallol and phloroglucinol are light-sensitive, the experiments involving these substances were conducted in the dark. The solutions were photolysed with pulses from a nitrogen laser (PTI PL 2300, 337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral density filters (*ca.* 5–25 $\mu\text{J pulse}^{-1}$ at the cell, flux $<40 \text{ J m}^{-2}$). Each pulse produced photolysis of di-*tert*-butyl peroxide, generating *tert*-butoxy radicals (which in turn abstracted the hydroxylic hydrogen from the hydroxyphenol), and induced a volume change in solution. This sudden volume change generated an acoustic wave that was detected by a piezoelectric transducer (Panametrics V101, 0.5 MHz) in contact with the bottom of the cell. The signals were amplified (Panametrics 5662) and measured by a digital oscilloscope (Tektronix 2430A). The signal-to-noise ratio was improved by averaging 32 acquisitions for each data point obtained at a given laser energy. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched (typically within less than 7% absorbance units at 337.1 nm) solution of *ortho*-hydroxybenzophenone (in the same mixtures but without the peroxide),¹⁰ which dissipates all of the absorbed energy as heat ($\phi_{\text{obs}} = 1$). For each run (experiment or calibration), four data points were collected, corresponding to four different laser intensities obtained using neutral density filters. The resulting waveforms from each data point were recorded for subsequent mathematical analysis, affording two waveforms for each point: sample and calibration. The analysis involved, for each laser energy, first the normalization of both waveforms and then their deconvolution using the software Sound Analysis by Quantum Northwest.¹¹

The basis of photoacoustic calorimetry has also been widely discussed before,^{4,7,8,12} and only the main equations needed for the calculations are presented here. For a two-step reaction

scheme, where the first one is induced by the laser pulse and the second involves the thermal reaction between a photochemically produced species and a substrate, the enthalpies are respectively given by:

$$\Delta_r H_1 = \frac{E_m - \Delta_{\text{obs}} H_1}{\Phi_r} + \frac{\Delta_r V_1}{\chi} \quad (1)$$

$$\Delta_r H_2 = \frac{-\Delta_{\text{obs}} H_2}{\Phi_r} + \frac{\Delta_r V_2}{\chi} \quad (2)$$

In these equations $E_m = N_A h\nu$ represents the molar photon energy and Φ_r is the reaction quantum yield. $\Delta_{\text{obs}} H_1$ and $\Delta_{\text{obs}} H_2$ correspond to the observed (or apparent) enthalpy changes and are calculated by multiplying E_m by $\phi_{\text{obs},1}$ and $\phi_{\text{obs},2}$, respectively. These parameters are the apparent fractions of photon energies released as heat, obtained from a deconvolution procedure of the sound waves.¹¹ Finally, the last two terms of eqns. (1) and (2) reflect a reaction volume correction due to the differences between the partial molar volumes of the reactants and products:¹³ $\Delta_r V_1$ and $\Delta_r V_2$ are the molar volume changes of the first and second step, respectively, and χ is the adiabatic expansion coefficient of the solvent.

Materials

Acetonitrile (Aldrich) was of HPLC grade and used as received. Di-*tert*-butyl peroxide (Aldrich) was purified according to a literature procedure.¹⁴ Phenol (Aldrich, 99+%) was sublimed in vacuum and kept under nitrogen prior to use. Catechol (Aldrich, 99+%) was purified by sublimation. Phloroglucinol (Aldrich, 99%) and pyrogallol (Aldrich, 99+%) were used as received. *ortho*-Hydroxybenzophenone (Aldrich) was recrystallized twice from an ethanol–water mixture.

Theoretical calculations

Density functional theory (DFT) calculations were carried out for hydroxyphenols and their phenoxy radicals in the gas phase with the Barone and Adamo's Becke style one parameter functional, using a modified Perdew-Wang exchange (MPW1)¹⁵ and Perdew-Wang 91 correlation,¹⁶ (MPW1-PW91).¹⁷ Total energies (E) were obtained from eqn. (3),¹⁸ where V_{NN} is the nuclear–nuclear interaction, H^{CORE} is a mono-electronic contribution to the total energy, including electron kinetic and electron–nuclear interaction energies, and V_{ee} is the coulombic interaction between the electrons.

$$E = V_{\text{NN}} + H^{\text{CORE}} + V_{\text{ee}} + E_{\text{X}}[\rho] + E_{\text{C}}[\rho] \quad (3)$$

The terms $E_{\text{X}}[\rho]$ and $E_{\text{C}}[\rho]$ represent the exchange and correlation energies, respectively, functionals of the electronic density ρ . The geometries were fully optimised with the Dunning double zeta correlation consistent basis set, including diffuse functions (aug-cc-pVDZ).¹⁹ Vibrational frequency analysis was used to confirm that stationary points were minimum energy structures and to calculate zero point energy (ZPE) corrections. A complete basis set procedure (CBS-4M)²⁰ was also applied to analyze the energetics of the gas-phase O–H bond dissociation and intramolecular hydrogen bonding in hydroxyphenols. This composite method was selected because it represents an excellent compromise between accuracy and computational effort. In addition, the phenol O–H bond dissociation enthalpy, $DH^\circ(\text{PhO–H})$, predicted by CBS-4M (375.4 kJ mol^{-1})²¹ is in good agreement with the recommended experimental value ($371.3 \pm 2.3 \text{ kJ mol}^{-1}$).^{2a} All the calculations were performed with the Gaussian-98 Program,²² and all the results (given as ESI⁺) were corrected with the zero point energies and with thermal corrections to 298 K.

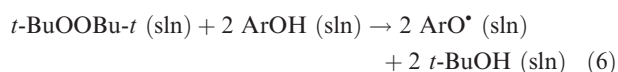
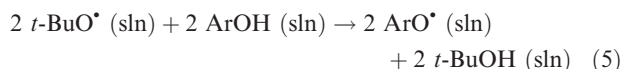
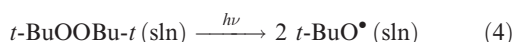
Basis set superposition error (BSSE) for the DFT calculations are quite small and were not included.²³ On the other

hand, CBS-4M calculations are based on a multilevel extrapolation procedure, which, in principle, minimizes finite basis set errors.

Results and discussion

Solution-phase bond dissociation enthalpies

The set of reactions that were examined by photoacoustic calorimetry are shown in eqns. (4)–(6). A *tert*-butoxy radical generated from the photolysis of di-*tert*-butyl peroxide (reaction (4)) abstracts a hydrogen atom from the phenolic substrate, yielding a phenoxy radical (reaction (5)). Reaction (6) represents the net process.



The TR-PAC technique allows the independent determination of the enthalpies of reactions (4) and (5) as described above. Deconvolution of the photoacoustic waveforms obtained in this case affords the amplitudes (ϕ_{obs}) of the two expected sequential processes and the lifetime (τ) of the second, according to the two elementary steps in reactions (4)–(6).^{12c} In the present case, we are only interested in the enthalpy of reaction (5) ($\Delta_r H_2$), which can be calculated from eqn. (2),²⁴ assuming that the volume change for this reaction is negligible, *i.e.* $\Delta_r V_2 = 0$.^{4,5,8} As the enthalpy of reaction (5) is simply twice the difference between the O–H bond dissociation enthalpies in the phenolic compound and *tert*-butyl alcohol in solution, $DH_{\text{sln}}^\circ(\text{ArO–H})$ can be derived from eqn. (7).

$$DH_{\text{sln}}^\circ(\text{ArO–H}) = \Delta_r H_2 / 2 + DH_{\text{sln}}^\circ(t\text{-BuO–H}) \quad (7)$$

The O–H bond dissociation enthalpy of *tert*-butyl alcohol in acetonitrile, $DH_{\text{sln}}^\circ(t\text{-BuO–H}) = 462.7 \pm 3.5 \text{ kJ mol}^{-1}$, was derived from eqn. (8):

$$\begin{aligned} DH_{\text{sln}}^\circ(t\text{-BuO–H}) &= \Delta_f H^\circ(t\text{-BuO}^\bullet, \text{sln}) + \Delta_f H^\circ(\text{H}^\bullet, \text{sln}) \\ &\quad - \Delta_f H^\circ(t\text{-BuOH}, \text{sln}) \\ &= DH_{\text{sln}}^\circ(t\text{-BuO–OBu-}t) / 2 \\ &\quad + [\Delta_f H^\circ(t\text{-BuOOBu-}t, 1) \\ &\quad + \Delta_{\text{sln}} H^\circ(t\text{-BuOOBu-}t, 1)] / 2 \\ &\quad + \Delta_f H^\circ(\text{H}^\bullet, \text{g}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) \\ &\quad - \Delta_f H^\circ(t\text{-BuOH}, 1) \\ &\quad - \Delta_{\text{sln}} H^\circ(t\text{-BuOH}, 1) \end{aligned} \quad (8)$$

where the O–O bond dissociation enthalpy of di-*tert*-butyl peroxide in acetonitrile ($156.8 \pm 6.3 \text{ kJ mol}^{-1}$), together with the solution enthalpies of di-*tert*-butyl peroxide ($5.5 \pm 0.2 \text{ kJ mol}^{-1}$) and *tert*-butyl alcohol ($10.2 \pm 0.5 \text{ kJ mol}^{-1}$) were taken

from a previous work.²⁵ The enthalpies of formation of liquid di-*tert*-butyl peroxide ($-380.9 \pm 0.9 \text{ kJ mol}^{-1}$), liquid *tert*-butyl alcohol ($-359.2 \pm 0.8 \text{ kJ mol}^{-1}$), and the hydrogen atom ($217.998 \pm 0.006 \text{ kJ mol}^{-1}$) were taken from the literature.^{14,26,27} Finally, an estimate for the solvation enthalpy of the hydrogen atom in organic solvents, $\Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) = 5 \pm 1 \text{ kJ mol}^{-1}$,^{2a} was used. This estimate is in keeping with a value of 5.8 kJ mol^{-1} , recently obtained from Monte Carlo calculations.²³

The experimental results obtained for $\Delta_{\text{obs}} H_2$, $\Delta_r H_2$ and $DH_{\text{sln}}^\circ(\text{ArO–H})$ are displayed in Table 1.

Gas-phase bond dissociation enthalpies (ECW method)

The relationship between solution- and gas-phase bond dissociation enthalpies is established in Scheme 1 (or eqn. (9)) through the enthalpies of solvation of the species involved.

$$\begin{aligned} DH^\circ(\text{ArO–H}) &= DH_{\text{sln}}^\circ(\text{ArO–H}) + \Delta_{\text{sln}} H^\circ(\text{ArOH}, \text{g}) \\ &\quad - \Delta_{\text{sln}} H^\circ(\text{ArO}^\bullet, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) \end{aligned} \quad (9)$$

Eqn. (9) is difficult to apply because the solvation enthalpies of the aryloxy radicals are not experimentally available.²⁸ The problem can, however, be avoided by assuming that, in a first approximation, the difference $\Delta_{\text{sln}} H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{ArO}^\bullet, \text{g})$ is simply given by the enthalpy of the H-bond between the phenolic compound and the solvent.⁵ This enthalpy can be estimated with the ECW model, by considering $\Delta H(\text{ECW}) = \Delta_{\text{sln}} H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{ArO}^\bullet, \text{g})$ (Table 2). The ECW model, developed by Drago and coworkers,²⁹ contains four parameters that reflect electrostatic (E_A , E_B) and covalent (C_A , C_B) contributions to the enthalpies of donor–acceptor interactions. Donor (B) and acceptor (A) parameters, optimized by a large database of experimentally determined enthalpies, are available for many substances.²⁹

The previous methodology yields absolute gas-phase values of ArO–H bond dissociation enthalpies. However, we are also interested in probing substituent effects on the energetics of that bond. This is better seen by deriving the ArO–H bond dissociation enthalpies *relative* to the O–H bond dissociation enthalpy in phenol, $\Delta DH^\circ(\text{ArO–H})$. These quantities are defined by eqn. (10),

$$\Delta DH^\circ(\text{ArO–H}) = DH^\circ(\text{ArO–H}) - DH^\circ(\text{PhO–H}) \quad (10)$$

and can be related to the corresponding quantities in solution, $\Delta DH_{\text{sln}}^\circ(\text{ArO–H})$, through eqn. (11):

$$\begin{aligned} \Delta DH^\circ(\text{ArO–H}) &= \Delta DH_{\text{sln}}^\circ(\text{ArO–H}) \\ &\quad + [\Delta_{\text{sln}} H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{ArO}^\bullet, \text{g})] \\ &\quad - [\Delta_{\text{sln}} H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{PhO}^\bullet, \text{g})] \end{aligned} \quad (11)$$

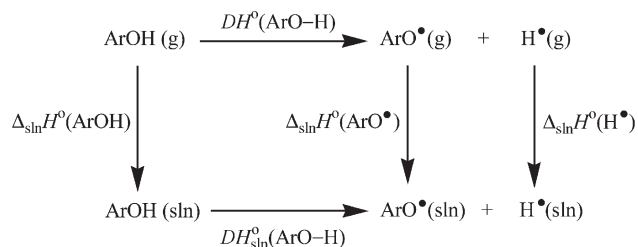
This equation has two advantages: (1) any error caused by application of the ECW model in estimating each one of the bracketed terms is likely to cancel; (2) the experimental uncertainties affecting the values of $\Delta DH_{\text{sln}}^\circ(\text{ArO–H})$ (and therefore

Table 1 TR-PAC results for the solution-phase (acetonitrile) O–H bond dissociation enthalpies in phenol and hydroxyphenols, $DH_{\text{sln}}^\circ(\text{ArO–H})$

| Molecule | Concentration/M | $\Delta_{\text{obs}} H_2^a / \text{kJ mol}^{-1}$ | $-\Delta_r H_2^{b,c} / \text{kJ mol}^{-1}$ | $DH_{\text{sln}}^\circ(\text{ArO–H})^{c,d} / \text{kJ mol}^{-1}$ |
|---|-----------------|--|--|--|
| PhOH | 0.1 | 131.8 ± 2.1 | 148.1 ± 2.1 | 388.7 ± 3.7 |
| 1,2-C ₆ H ₄ (OH) ₂ | 0.006 | 180.0 ± 7.6 | 202.3 ± 7.6 | 361.6 ± 5.2 |
| 1,2,3-C ₆ H ₃ (OH) ₃ | 0.003 | 210.2 ± 8.5 | 236.2 ± 8.5 | 344.6 ± 5.5 |
| 1,3,5-C ₆ H ₃ (OH) ₃ | 0.01 | 134.6 ± 7.2 | 151.2 ± 7.2 | 387.1 ± 5.0 |

^a Measured enthalpy change for the sequential slower process, attributed to reaction (5). Each value of $\Delta_{\text{obs}} H_2$ represents the average of at least five independent results. The uncertainties are twice the standard deviation of the mean in each case. ^b Enthalpy of reaction (5). ^c The uncertainties do not include the error in the quantum yield (which nearly cancels out when relative bond dissociation enthalpies are derived; see Table 2).

^d Calculated from eqn. (7) with $DH_{\text{sln}}^\circ(t\text{-BuO–H}) = 462.7 \pm 3.5 \text{ kJ mol}^{-1}$ (see text).



Scheme 1

of $\Delta DH^\circ(\text{ArO-H})$) are *smaller* than the uncertainties assigned to the respective absolute values. The reason is simple to understand: there are several auxiliary data needed to derive the absolute values of ArO-H bond dissociation enthalpies, but these data cancel out when the relative values are calculated through eqn. (12):

$$\Delta DH_{\text{sln}}^\circ(\text{ArO-H}) = \Delta_r H_2/2 - \Delta_r H'_2/2 \quad (12)$$

Here, $\Delta_r H_2/2$ and $\Delta_r H'_2/2$ are the enthalpies of reaction (5) for ArOH and PhOH, respectively.

The results for $\Delta DH_{\text{sln}}^\circ(\text{ArO-H})$ and $\Delta DH^\circ(\text{ArO-H})$ are summarized in Table 2. Note that a negative value represents a weakening of the O-H bond, *i.e.* our results indicate that the O-H bond in the phenolic compound is destabilized by the addition of a hydroxy group in any position of the ring, both in acetonitrile and in the gas phase.

The relative bond dissociation enthalpy for catechol is in keeping with the value selected in a recent review, -30 ± 8 kJ mol^{-1} ,^{2a} which relies on a study by Suryan *et al.*³⁰ These authors used very low-pressure pyrolysis (VLPP) to determine the activation energies for the decomposition of a series of substituted anisoles, $\text{XC}_6\text{H}_4\text{OCH}_3$ ($\text{X} = \text{H}, \text{OH}, \text{CH}_3, \text{OCH}_3$, *etc.*), and assumed that the differences in the activation energies are identical to the differences in $\text{XC}_6\text{H}_4\text{O-CH}_3$ bond dissociation enthalpies. Moreover, they suggested that the trends in $\text{XC}_6\text{H}_4\text{O-CH}_3$ and in $\text{XC}_6\text{H}_4\text{O-H}$ bond dissociation enthalpies are similar. This procedure led to $\Delta DH^\circ(2\text{-OHC}_6\text{H}_4\text{O-H}) = -30.1$ kJ mol^{-1} (no uncertainty was indicated), a value that is fairly close to the result of Austin model 1 semi-empirical calculations (AM1) by the same group, -25.1 kJ mol^{-1} .^{30a} The issue of parallel trends between $\text{XC}_6\text{H}_4\text{O-CH}_3$ and $\text{XC}_6\text{H}_4\text{O-H}$ was further discussed by Pratt *et al.*³¹ These authors have also reported VLPP results for 2-methoxyphenol (guaiacol), which are in excellent agreement with those by Suryan *et al.* Finally, a recent estimate using a correlation between experimental O-H bond dissociation enthalpies and kinetic data, afforded $\Delta DH^\circ(2\text{-OHC}_6\text{H}_4\text{O-H}) = -28.9$ kJ mol^{-1} ,³² matching the value in Table 2.

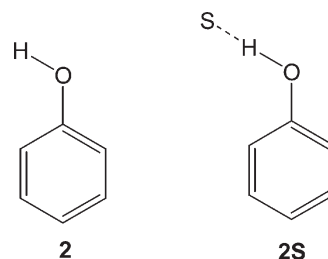
To our knowledge there are no literature values for the experimental O-H bond dissociation enthalpies in pyrogallol and in phloroglucinol. Our results indicate that a substantial weakening effect of the O-H bond (44 kJ mol^{-1}) occurs when

three hydroxy groups occupy neighboring positions, and that almost no effect is observed when the same substituents occupy positions 3 and 5.

The gas-phase PhO-H bond dissociation enthalpy

As described above, the gas-phase bond dissociation enthalpies given in Table 2 are *relative* values, derived from TR-PAC solution data using reasonable assumptions regarding the solvation energetics of the species involved. To calculate absolute data one needs the value of the gas-phase O-H bond dissociation enthalpy in phenol. The question is, which value should be used? Taking $DH_{\text{sln}}^\circ(\text{PhO-H})$ and $\Delta H(\text{ECW})$ from Tables 1 and 2, together with $\Delta_{\text{sln}}H^\circ(\text{H}^\bullet, \text{g}) = 5 \pm 1$ kJ mol^{-1} ,^{2a} we obtain from eqn. (9) $DH^\circ(\text{PhO-H}) = 365.0 \pm 3.8$ kJ mol^{-1} . However, this value is some 6 kJ mol^{-1} lower than the one recommended in ref. 2(a) (371.3 ± 2.3 kJ mol^{-1}), which is a weighted average of the results from several experimental gas-phase studies. The discrepancy with a computational chemistry study at the G3(MP2) level, which afforded $DH^\circ(\text{PhO-H}) = 376.1$ kJ mol^{-1} , is even higher.²¹ Therefore, although 6 kJ mol^{-1} can be regarded as a fairly small disagreement, it suggests that either the TR-PAC experiments are not accurate enough or that the estimation method of the solvation energetics should be improved. Since we had no reason to challenge our photoacoustic results,³³ we decided to use quantum chemistry calculations to test the basic assumption of that method, *i.e.* to check if the difference $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g})$ can be identified with the enthalpy of the H-bond between phenol and the solvent.⁵ As a first approximation, we have considered that the solvated species (PhOH and PhO[•]) can be modeled by gas-phase “complexes” involving a single solvent molecule (see, however, below).

The computed ground state energies of phenol (**2**), acetonitrile (**S**), and a phenol-acetonitrile complex (**2S**) (see also Fig. 1(a)), led to 23.1 kJ mol^{-1} for the enthalpy of the H-bond between PhOH and the solvent (Table 3). This value can be compared with a recently calculated B3LYP result (24.6 kJ mol^{-1}),³⁴ with an experimental value recommended in a careful study by Lopes and Thompson (21.8 kJ mol^{-1}),³⁵ with a literature evaluation by Wayner *et al.* (19.7 kJ mol^{-1}),⁵ and with $-\Delta H(\text{ECW}) = 18.7$ kJ mol^{-1} (Table 2).



When the same exercise was carried out for the corresponding phenoxy radical (**2r** and **2rS**) we computed 12.4 kJ mol^{-1} for the phenoxy-acetonitrile interaction (Fig. 1(b)). Therefore,

Table 2 Solution- and gas-phase O-H bond dissociation enthalpies in hydroxyphenols relative to the O-H bond dissociation enthalpy in phenol^a

| Molecule | $\Delta DH_{\text{sln}}^\circ(\text{ArO-H})^b$ | ECW method | | Microsolvation method | |
|---|--|--------------------------|-----------------------------------|--|-----------------------------------|
| | | $\Delta H(\text{ECW})^c$ | $\Delta DH^\circ(\text{ArO-H})^d$ | $\Delta_{\text{sln}}H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{ArO}^\bullet, \text{g})^e$ | $\Delta DH^\circ(\text{ArO-H})^d$ |
| PhOH | 0 | -18.7 ± 1.0 | 0 | -10.7 | 0 |
| 1,2-C ₆ H ₄ (OH) ₂ | -27.1 ± 3.9 | -18.7 ± 1.0 | -27.1 ± 4.1 | -11.9 | -28.3 |
| 1,2,3-C ₆ H ₃ (OH) ₃ | -44.1 ± 4.4 | -18.7 ± 1.0 | -44.1 ± 4.6 | (-10.7) | -44.1 |
| 1,3,5-C ₆ H ₃ (OH) ₃ | -1.6 ± 3.8 | -19.1 ± 1.0 | -2.0 ± 4.1 | (-10.7) | -1.6 |

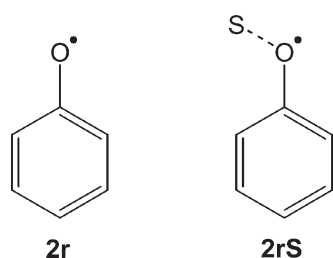
^a Values in kJ mol^{-1} . ^b Calculated through eqn. (12) with data from Table 1. ^c Enthalpy of hydrogen bond formation between the substituted phenol and acetonitrile estimated with the ECW model (see text). ^d Calculated with eqn. (11). ^e Calculated by the microsolvation method (see Table 3). Estimated values in parentheses.

Table 3 Summary of theoretical values for the inter- and intramolecular hydrogen bonds^a

| | -ΔH/kJ mol ⁻¹ | |
|----------------------------------|--------------------------|--------|
| | MPW1PW91 | CBS-4M |
| Intermolecular bonds | | |
| 2 + S → 2S | 23.1 | 20.1 |
| 2r + S → 2rS | 12.4 | 18.3 |
| 2 + 2rS → 2S + 2r ^b | 10.7 | 4.3 |
| 3 + S → 3S | 22.6 | |
| 3S + S → 3SS | 7.1 | |
| 3 + S + S → 3SS | 29.7 | |
| 3r + S → 3rS | 13.8 | |
| 3rS + S → 3rSS | (4) | |
| 3r + S + S → 3rSS | (17.8) | |
| 3 + 3rSS → 3SS + 3r ^c | 11.9 | |
| Intramolecular bonds | | |
| 3' → 3 | 15.5 | 17.3 |
| 3'r → 3r | 37.3 | 33.9 |
| 3'r + 3 → 3' + 3r ^d | 21.8 | 16.6 |
| 5' → 5 | 15.5 | 16.8 |
| 5'r → 5r | 62.8 | 65.9 |
| 5'r + 5 → 5' + 5r ^d | 47.3 | 49.1 |

^a Values calculated from the ground state energies, given as ESI. Estimated data in parentheses. ^b Identified with $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g})$. ^c Identified with $\Delta_{\text{sln}}H^\circ(3, \text{g}) - \Delta_{\text{sln}}H^\circ(3r, \text{g})$. ^d Difference between the intramolecular H-bond enthalpies in the radical and in the parent phenol (see text).

according to our microsolvation model, $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g}) = -10.7 \text{ kJ mol}^{-1}$ and thus the differential solvation enthalpy cannot be identified with the enthalpy of the H-bond between phenol and acetonitrile. Using these theoretical results together with $DH_{\text{sln}}^\circ(\text{PhO-H})$ from Table 1 and $\Delta_{\text{sln}}H^\circ(\text{H}^\bullet, \text{g}) = 5 \pm 1 \text{ kJ mol}^{-1}$,^{2a} we obtain from eqn. (9) $DH^\circ(\text{PhO-H}) = 373.0 \text{ kJ mol}^{-1}$, closer to the selected gas-phase value. Note that the structure 2rS merely indicates that an acetonitrile interacts with the phenoxy radical, which in fact is essentially a carbon-centered radical. The correct structure is shown in Fig. 1(b), where the acetonitrile interacts with the radical both through the nitrogen and a methyl hydrogen atom.



Our microsolvation model, considering a single solvent molecule, is obviously too simplistic. However, it indicates that the acetonitrile-phenoxy radical interaction is stronger than anticipated, and therefore that the solvation enthalpy of PhO[•] is not negligible. When the above exercise, involving only one acetonitrile, is repeated with the CBS-4M method, we obtain $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g}) = -4.3 \text{ kJ mol}^{-1}$. The small discrepancy with the DFT result is due to the fact that CBS-4M predicts a stronger interaction of phenoxy radical with acetonitrile (18.3 kJ mol⁻¹, compared with 12.4 kJ mol⁻¹ by DFT).

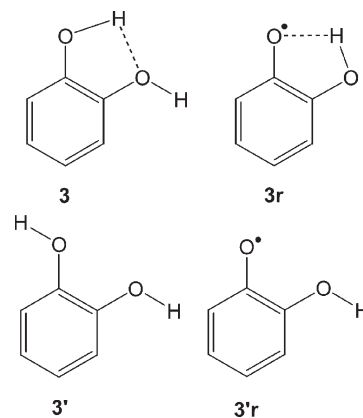
To further substantiate the statement that the solvation enthalpy of the phenoxy radical is not negligible, we have performed B3LYP calculations involving PhOH and PhO[•] clusters with two acetonitriles and also Monte Carlo

calculations using 500 solvent molecules.²³ The results from this study support the simple model above and our conclusion: the DFT calculations with two acetonitriles and the Monte Carlo results led, respectively, to $-11.4 \text{ kJ mol}^{-1}$ (at 0 K) and -2.5 kJ mol^{-1} (at 298 K) for $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g})$. It has been shown that the strong interaction between the phenoxy radical and acetonitrile is mainly due to a dipole-dipole interaction. The phenoxy radical has a much larger dipole moment than phenol.²³

In a recent paper, Bakalbassis *et al.*³⁶ have reported the O-H bond dissociation enthalpies of several phenols (including phenol itself, catechol and pyrogallol), computed at the UB3LYP level with a variety of basis sets. In the case of phenol, their "best" value is $DH^\circ(\text{PhO-H}) = 371.1 \text{ kJ mol}^{-1}$. The same authors also calculated the bond dissociation enthalpies in several solvents, using continuum models to account for the solvation. They recommend $DH_{\text{sln}}^\circ(\text{PhO-H}) = 382.9 \text{ kJ mol}^{-1}$ in acetonitrile. This implies that $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g}) = -6.8 \text{ kJ mol}^{-1}$, in keeping with the previous discussion.

Gas-phase bond dissociation enthalpies (microsolvation method) and intramolecular hydrogen bonds

Our microsolvation model and the computational tools allow to extend the previous discussion to the hydroxyphenols and dihydroxyphenols listed in Table 2. The case of catechol (3) is complicated by the intramolecular H-bond that occurs both in the parent compound and in the radical (3r). By comparing the DFT ground-state total energies of these species (Fig. 1(c) and (d)) with the energies of 3' and 3'r, where one OH group was rotated by 180°, we found that the enthalpy of the intramolecular bond in 3 and in 3r is, respectively, 15.5 and 37.3 kJ mol⁻¹, *i.e.* the H-bond is some 22 kJ mol⁻¹ stronger in the radical than in the parent catechol. The same exercise with the CBS-4M results led to 17.3 and 33.9 kJ mol⁻¹ for the intramolecular bonds in 3 and in 3r, respectively, leading to a difference of about 17 kJ mol⁻¹, in fair agreement with the DFT value.



Our values for the intramolecular H-bond in catechol (3) are comparable with other literature results obtained at several theory levels: 18.9 kJ mol⁻¹,³⁷ 21.2 kJ mol⁻¹,³⁶ 15.9 kJ mol⁻¹,^{38,39} 17.2 kJ mol⁻¹.⁴⁰ As stated in the Introduction, calculations by de Heer *et al.* led to 18.4 kJ mol⁻¹ for the intramolecular H-bond in 2-methoxyphenol (see 1S).^{2g} It should be noted, however, that several studies suggest that all the above theoretical values, based on the energy difference between the *trans* and the *cis*-conformers (*i.e.* 3' vs. 3 and 3'r vs. 3r), are overestimated.^{37,41-43}

Although the evaluation of the enthalpy of the intramolecular H-bond in catechol is important in itself, it is the difference between this enthalpy and the enthalpy of the intramolecular H-bond in the corresponding radical (3r) that is required for

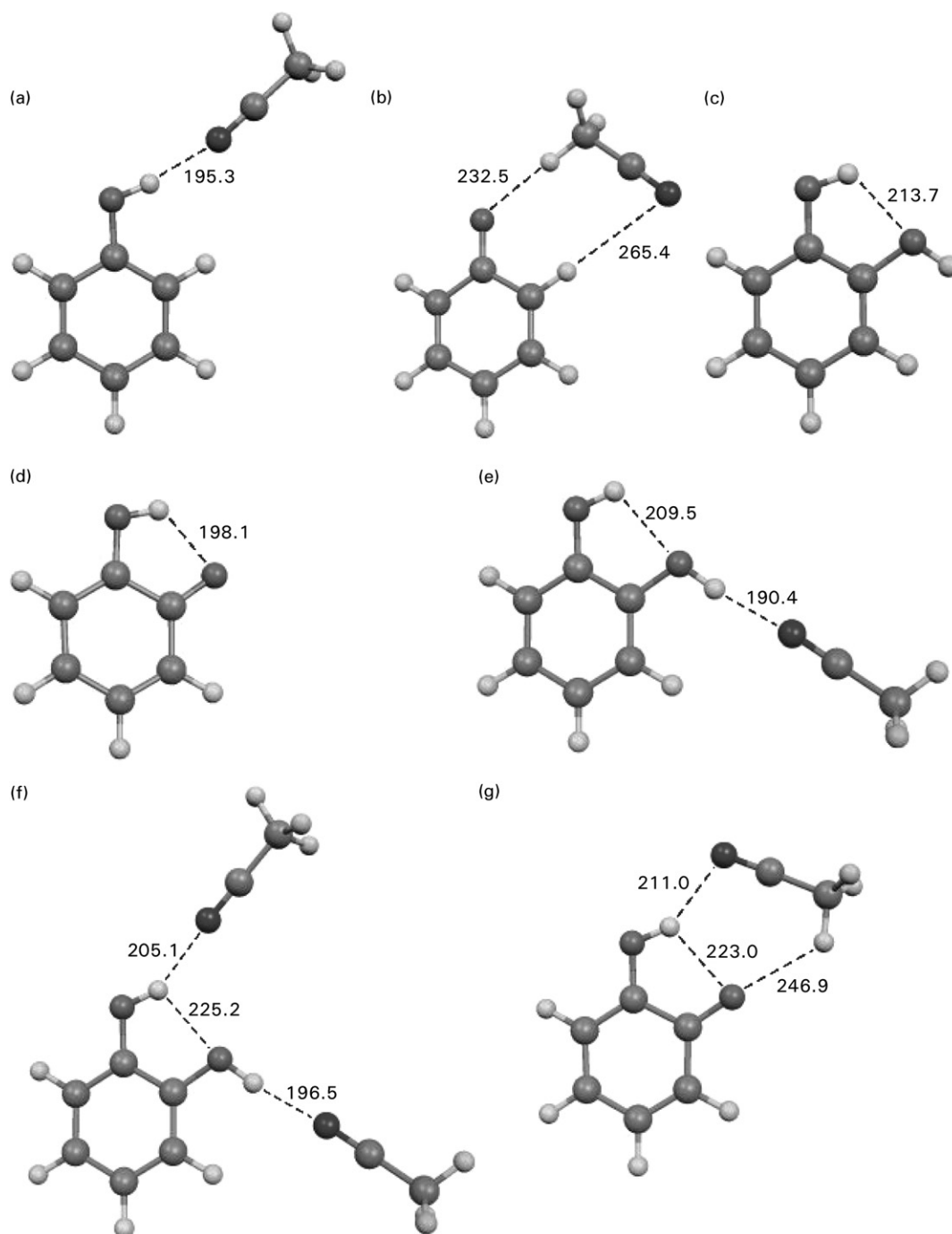
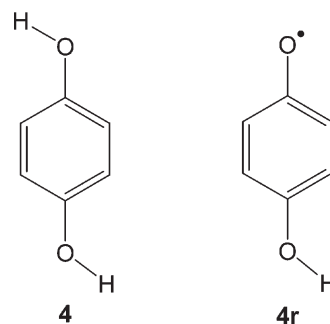


Fig. 1 DFT (MPW1PW91/aug-cc-pVDZ) computed structures of several phenolic compounds and complexes with acetonitrile discussed in the text. Distances in pm.

discussing the O–H bond dissociation enthalpy in **3**. As mentioned above, we obtained 37.3 kJ mol^{-1} (DFT) and 33.9 kJ mol^{-1} (CBS-4M) for the latter, values that compare with the one reported by Foti *et al.* (38.1 kJ mol^{-1}).³⁹ Therefore, we estimate that the difference between the H-bonds in catechol and its radical is either $-21.8 \text{ kJ mol}^{-1}$ (DFT) or $-16.6 \text{ kJ mol}^{-1}$ (CBS-4M). We shall accept these values, assuming that any error caused by the use of the *cis-trans* method cancels out when the difference is calculated. In fact, this hypothesis is supported by the values computed for the enthalpy of reaction (13) at the two theory levels, $-18.0 \text{ kJ mol}^{-1}$ (DFT) and $-12.6 \text{ kJ mol}^{-1}$ (CBS-4M), which is an isodesmic and isogyric process and therefore should not be affected by the problems raised about the use of the *cis-trans* approach.



It is well established that the O–H bond dissociation enthalpy in phenolic compounds can be estimated by considering the nature and the position of the substituents in the aromatic ring and by adding their contributions to the

weakening or strengthening of that bond.^{38,44} In the absence of steric effects and H-bonds, the electronic effects of *ortho*- and *para*-substituents on $DH^{\circ}(\text{ArO-H})$ should be similar. This is observed in the case of the hydroxy group, whose electronic contributions for the *ortho* and *para* positions are -21.7 and -24.7 kJ mol⁻¹, respectively,³⁸ *i.e.* both produce a decrease in $DH^{\circ}(\text{ArO-H})$. Hence, in the absence of H-bonds, reaction (13) should be *endothermic* by 3 kJ mol⁻¹. As we have computed -18.0 kJ mol⁻¹ using the DFT method, the difference between the intramolecular H-bonds in **3** and in **3r** is -21.0 kJ mol⁻¹, similar to the value obtained from the *cis-trans* method (-21.8 kJ mol⁻¹) using the same theory level. An identical conclusion is obtained with the CBS-4M results: the computed enthalpy of reaction (13) (-12.6 kJ mol⁻¹) corrected with the electronic effect yields -15.6 kJ mol⁻¹ for the difference between the intramolecular H-bonds in **3** and in **3r**, which is close to the value obtained above from the *cis-trans* method (-16.6 kJ mol⁻¹).

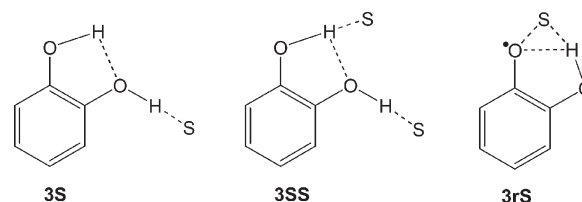
The larger intramolecular stabilization of **3r** relative to **3** is consistent with the fact that the computed gas-phase O-H bond dissociation enthalpy in catechol is lower than in hydroquinone (**4**) and, of course, phenol (**2**). The enthalpy of reaction (14), which measures the difference between the gas-phase O-H bond dissociation enthalpies in hydroquinone and phenol, $\Delta DH^{\circ}(\text{ArO-H})$, is calculated as -21.2 kJ mol⁻¹ (DFT) or -15.2 kJ mol⁻¹ (CBS-4M) (Table 4).



As bond dissociation enthalpies calculated from CBS-4M calculations are generally more accurate than those based on DFT methods,⁴⁵ we shall accept that, for hydroquinone, $\Delta DH^{\circ}(\text{ArO-H}) = -15.2$ kJ mol⁻¹. This should be compared with the selection made in an early review (-27 ± 10 kJ mol⁻¹),^{2a} based on several experimental^{30b,46} and theoretical values,^{30a,47} which range from -10.5 to -34.8 kJ mol⁻¹. The upper limit of this range, -10.5 kJ mol⁻¹, comes from the VLPP study by Suryan *et al.*^{30b} and the lower limit from an electrochemical study by Bordwell and Cheng in dimethyl sulfoxide.^{46a} Two other electrochemical studies in water led to -33.5 kJ mol⁻¹ and to -28.7 kJ mol⁻¹.^{46b,46c} The theoretical values derived with functional density methods, -22.6 kJ mol⁻¹,^{47a} and -26.5 kJ mol⁻¹,^{47b} are in good agreement with each other but slightly smaller than the AM1 value reported by Suryan *et al.*, -16.7 kJ mol⁻¹.^{30a}

Surprisingly, the solution-phase O-H relative bond dissociation enthalpy in catechol, $\Delta DH_{\text{sln}}^{\circ}(\text{ArO-H})$ (Table 2), is quite close to the gas-phase VLPP value, -30.1 kJ mol⁻¹.^{30b} To clarify this agreement, we turned to our simple microsolvation model, by introducing one acetonitrile at a time (**3S** and **3SS**; see also Fig. 1(e) and (f)). According to our calculations,

the first intermolecular bond (22.6 kJ mol⁻¹) is significantly stronger than the second (7.1 kJ mol⁻¹). As expected, the enthalpy of the first intermolecular bond is similar to the one given above for phenol (23.1 kJ mol⁻¹). The second intermolecular bond is weaker because the acetonitrile binds to an hydrogen that is already involved in the intramolecular bond. The same exercise for the radical (**3rS**; Fig. 1(g)) led to 13.8 kJ mol⁻¹. Note in Fig. 1(g) that the acetonitrile is interacting both with the phenolic hydrogen and with the oxygen radical center. When we attempted to optimize the structure of **3r** with two acetonitriles, we were not able to find the energy minimum at our calculation level, probably reflecting a rather weak interaction between **3rS** and the second solvent molecule. In fact, our results for phenoxy radical bound to one and two acetonitriles, obtained at different calculation levels, indicate that the interaction of the second acetonitrile is only *ca.* 4 kJ mol⁻¹.²³ The net interaction of two acetonitriles with the parent compound (29.7 kJ mol⁻¹) is thus stronger than the net interaction with the radical (17.8 kJ mol⁻¹), the difference being -11.9 kJ mol⁻¹, which we identify as $\Delta_{\text{sln}}H^{\circ}(\mathbf{3}, \text{g}) - \Delta_{\text{sln}}H^{\circ}(\mathbf{3r}, \text{g})$. As noted in Table 2, this value is quite close to the one obtained for phenol. Therefore, using eqn. (11), $\Delta DH_{\text{sln}}^{\circ}(\text{ArO-H}) \approx \Delta DH^{\circ}(\text{ArO-H})$.



Lucarini *et al.* used equilibrium experiments in benzene to derive the O-H bond dissociation enthalpies of 3,5-di-*tert*-butylcatechol and 2,5-di-*tert*-pentylhydroquinone.^{2b} The values relative to the O-H bond dissociation enthalpy in phenol, -34.7 kJ mol⁻¹ and -28.5 kJ mol⁻¹, respectively, are not strictly comparable with those for catechol (**3**) and hydroquinone (**4**), which have no other ring substituents. However, we can predict the relative O-H bond dissociation enthalpies in these two phenols by correcting the above experimental values for the effect of the substituents through the additivity method.^{2a,38} We shall use the corrections given by Lucarini *et al.*^{2b} The net effect of two *tert*-butyl groups in the *ortho* and *para* positions is -15.3 kJ mol⁻¹, leading to $-34.7 + 15.3 = -19.4$ kJ mol⁻¹ for the relative O-H bond dissociation enthalpy in **3**. On the other hand, the net effect of two *tert*-pentyl groups in the *ortho* and *meta* positions is estimated as -9.4 kJ mol⁻¹, leading to $-28.5 + 9.4 = -19.1$ kJ mol⁻¹ for the relative O-H bond dissociation enthalpy in **4**.

The fact that the results by Lucarini *et al.* lead to almost identical values for the O-H bond dissociation enthalpy in catechol (**3**) and in hydroquinone (**4**) is surprising, considering the computed enthalpy of reaction (13), -12.6 kJ mol⁻¹ (CBS-4M).⁴⁸ Recall that this enthalpy is identified with the difference between the O-H bond dissociation enthalpies in catechol and in hydroquinone. In addition, we would expect that, for example, $\Delta DH_{\text{sln}}^{\circ}(\text{ArO-H})$ for catechol in benzene (*ca.* -19 kJ mol⁻¹) were closer to the VLPP gas-phase result (-30.1 kJ mol⁻¹) or the TR-PAC value in Table 2, which are in close agreement. Moreover, the enthalpy of reaction (15), which is identified with $\Delta DH^{\circ}(\text{ArO-H})$ (see Table 4) for catechol (**3**), is computed as -27.8 kJ mol⁻¹ (CBS-4M), also in keeping with the data in Table 2. It is also important to note that the DFT method leads to -39.2 kJ mol⁻¹ for the enthalpy of reaction (15).⁴⁹ This result suggests that bond dissociation enthalpies computed with MPW1PW91/aug-cc-pDVZ and other DFT methods, particularly if the molecules investigated have intramolecular H-bonds, should be regarded with caution, even when isodesmic and isogyric reactions are used to derive the

Table 4 Summary of experimental and theoretical gas-phase O-H bond dissociation enthalpies in phenol and hydroxyphenols^a

| Molecule | $DH^{\circ}(\text{ArO-H})$ | | |
|---|----------------------------|---------------|---------------|
| | Exptl. ^b | MPW1PW91 | CBS-4M |
| PhOH | 373.0 ^c (0) | 343.2 (0) | 375.4 (0) |
| 1,2-C ₆ H ₄ (OH) ₂ | 344.7 (-28.3) | 304.0 (-39.2) | 347.6 (-27.8) |
| 1,4-C ₆ H ₄ (OH) ₂ | | 322.0 (-21.2) | 360.2 (-15.2) |
| 1,2,3-C ₆ H ₃ (OH) ₃ | 328.9 (-44.1) | 280.1 (-63.0) | 322.2 (-53.2) |
| 1,3,5-C ₆ H ₃ (OH) ₃ | 371.4 (-1.6) | 347.1 (3.9) | 374.4 (-1.0) |

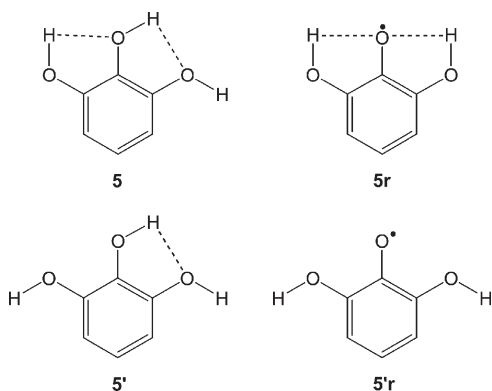
^a Values in kJ mol⁻¹. Data in parentheses are the bond dissociation enthalpies relative to phenol. ^b Calculated with $\Delta DH^{\circ}(\text{ArO-H})$ data from the microsolvation method in Table 2 and $DH^{\circ}(\text{PhO-H}) = 373.0$ kJ mol⁻¹. Data from Table 2. ^c Calculated with eqn. (9) from the solution value in Table 1 (see text).

results (see also below).



Bakalbassis *et al.* computed $\Delta DH^\circ(\text{ArO-H}) = -28.7 \text{ kJ mol}^{-1}$ and $\Delta DH_{\text{sln}}^\circ(\text{ArO-H}) = -25.6 \text{ kJ mol}^{-1}$ (in acetonitrile), both in very good agreement with our values in Table 2 and also with the CBS-4M result mentioned above (Table 4).³⁶

The introduction of a second *ortho*-hydroxy group in the benzene ring (pyrogallol, **5**) causes an additional decrease of 17 kJ mol^{-1} in $\Delta DH_{\text{sln}}^\circ(\text{ArO-H})$. The value shown in Table 2, $-44.1 \pm 4.4 \text{ kJ mol}^{-1}$, is comparable to the one observed in α -tocopherol ($-43 \pm 4 \text{ kJ mol}^{-1}$).^{2a} Calculations using the *cis-trans* method predict that the energy difference between **5'** and **5** is 15.5 kJ mol^{-1} (DFT) or 16.8 kJ mol^{-1} (CBS-4M) – values that are similar to the ones obtained above for catechol (**3'** and **3**). This stabilization of the parent phenol is, however, offset by the energy difference between **5'r** and **5r**, computed as 62.8 kJ mol^{-1} (DFT) or 65.9 kJ mol^{-1} (CBS-4M).



Equilibrium studies in *tert*-butyl alcohol by Lucarini *et al.* led to $\Delta DH_{\text{sln}}^\circ(\text{ArO-H}) = -20.9 \text{ kJ mol}^{-1}$ and $-21.3 \text{ kJ mol}^{-1}$ for propyl gallate and octyl gallate, respectively. As the *para*-COOR group is an electron acceptor it strengthens the O–H bond. This strengthening can be estimated from a linear plot between relative O–H bond dissociation enthalpies and the Hammett parameter σ^+ .^{2a} Using $\sigma_p^+(\text{COOR}) = 0.48$,⁵⁰ one obtains $\Delta DH^\circ(\text{ArO-H}) = 12.6 \text{ kJ mol}^{-1}$. Therefore, the above results and this estimate indicate that $\Delta DH_{\text{sln}}^\circ(\text{ArO-H})$ in pyrogallol should be about -34 kJ mol^{-1} .

As in the case of catechol, where our TR-PAC result for $\Delta DH^\circ(\text{ArO-H})$ is *ca.* 9 kJ mol^{-1} lower than the value derived from the study by Lucarini *et al.*, for pyrogallol the difference is very similar (10 kJ mol^{-1}). It is also important to note that the DFT calculations (see Table 4) lead to $-63.0 \text{ kJ mol}^{-1}$ for the enthalpy of reaction (16), *i.e.* there is again a significant discrepancy between the DFT and the solution-derived value.⁵¹ The CBS-4M result ($-53.2 \text{ kJ mol}^{-1}$, Table 4) is, however, in much better agreement, although not perfect, with the value in Table 2.



The differential solvation of pyrogallol and its radical should not justify the 10 kJ mol^{-1} discrepancy between the TR-PAC and the CBS-4M results. In fact, based on the values obtained above for the binding energies with acetonitrile, estimated from **3S**, **3SS** and **3rS**, we predict that the solvation of **5** and **5r** are *ca.* -39 and -28 kJ mol^{-1} , respectively, implying that $[\Delta_{\text{sln}}H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{ArO}^\bullet, \text{g})] \approx -11 \text{ kJ mol}^{-1} \approx [\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\bullet, \text{g})]$ (see eqn. (11)) and $\Delta DH_{\text{sln}}^\circ(\text{ArO-H}) \approx \Delta DH^\circ(\text{ArO-H})$.

Interestingly, the value of $\Delta DH^\circ(\text{ArO-H})$ computed by Bakalbassis *et al.* for pyrogallol, $-47.2 \text{ kJ mol}^{-1}$,³⁶ is in better agreement with the experimentally derived result in Table 2 than the value obtained by the CBS-4M method (Table 4).

The results displayed in the last row of Table 2 are for phloroglucinol. In this case it is obvious that the solvation effects should be quite similar to those derived for the pair phenol–phenoxy radical, and therefore $\Delta DH_{\text{sln}}^\circ(\text{ArO-H}) \approx \Delta DH^\circ(\text{ArO-H})$. Considering the experimental uncertainty, we conclude that *meta*-OH substituents have a negligible effect on the O–H bond dissociation enthalpy, which is in keeping with early knowledge.^{2a} The theoretical calculations agree with the experimental result (Table 4): $\Delta DH^\circ(\text{ArO-H}) = -1.0 \text{ kJ mol}^{-1}$ (CBS-4M).

Table 3 summarizes the theoretical values derived in the present work for the intra- and intermolecular hydrogen bonds. Finally, Table 4 collects the experimental and theoretical data obtained for the gas-phase O–H bond dissociation enthalpies. The disagreement between DFT and the remaining values is apparent.

Conclusions

Time-resolved photoacoustic calorimetry is a useful tool for probing the energetics of phenolic O–H bonds in solution, particularly when the hydrogen abstraction reactions (yielding the phenoxy radicals) are too slow to be examined by classical photoacoustic calorimetry. Our results in acetonitrile show that the introduction of one and two hydroxy groups at the *ortho*-positions of the phenolic ring, respectively, yield decreases of 27 and 44 kJ mol^{-1} in the O–H bond dissociation enthalpy, relative to the O–H bond dissociation enthalpy in phenol.

A microsolvation model relying on DFT (MPW1PW91/aug-cc-pVDZ) calculations was used to estimate the differences between the solvation enthalpies of each one of the parent phenols and its radical. The results indicate that these differential solvation enthalpies are smaller than previously accepted because the radicals have strong interactions with the solvent. However, the differential solvation enthalpies are similar for all the phenols investigated (including phenol itself), implying that the solution-phase values of the O–H bond dissociation enthalpies relative to the same quantities in phenol, $\Delta DH_{\text{sln}}^\circ(\text{ArO-H})$, are close to the corresponding gas-phase results, $\Delta DH^\circ(\text{ArO-H})$. The assumption $\Delta DH_{\text{sln}}^\circ(\text{ArO-H}) \approx \Delta DH^\circ(\text{ArO-H})$ (whose associated error in acetonitrile is quite small) probably can be generalized to other solvents. A direct result from this conclusion is that to calculate *absolute* values of gas-phase bond dissociation enthalpies in substituted phenols from $\Delta DH_{\text{sln}}^\circ(\text{ArO-H})$ and $DH_{\text{sln}}^\circ(\text{PhO-H})$ data, the solvation enthalpies of ArOH and ArO[•] are not required: only the solvation enthalpies of phenol and phenoxy radical are needed to evaluate $DH^\circ(\text{PhO-H})$ in eqn. (10).

As indicated by our photoacoustic calorimetry results and also by CBS-4M calculations, the DFT method seems to underestimate O–H bond dissociation enthalpies in compounds containing intramolecular H-bonds, even when isodesmic and isogyric reactions are used.

Acknowledgements

This work was supported by Fundação para a Ciência e Tecnologia, Portugal (grants POCTI/35406/QUI/1999 and POCTI/43315/QUI/2001). C. F. C. and R. C. G. thank Fundação para a Ciência e a Tecnologia, for PhD grants (SFRH/BD/6519/2001 and PRAXIS XXI/BD/15920/98, respectively).

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