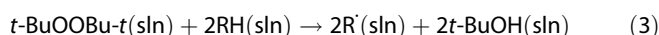
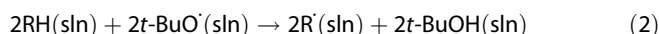
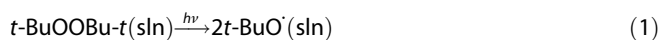


Reaction of *para*-Hydroxy-Substituted Diphenylmethanes with *tert*-Butoxy Radical

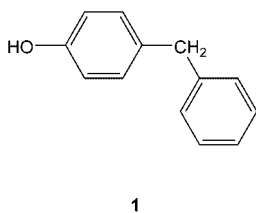
Catarina F. Correia,^[a] Rui M. Borges dos Santos,^{*,[b]} Sílvia G. Estácio,^[a, c] João P. Telo,^[d] Benedito J. Costa Cabral,^[a, c] and José A. Martinho Simões^{*,[a]}

Introduction

Substituent effects on bond dissociation enthalpies of aromatic compounds, such as phenols,^[1] anisoles,^[2] and methyl benzenes,^[2a,3] have been profusely investigated in the recent past. Many of these studies rely on photoacoustic calorimetry (PAC) experiments, which afford solution-phase bond dissociation enthalpies.^[4] These quantities can then be related to gas-phase values (see below). The general approach is illustrated in Equations (1)–(3), where Equation (3) is the net reaction. The photochemically produced *tert*-butoxy radical (*t*-BuO[•]) is employed to abstract a hydrogen atom from the molecule of interest (RH), yielding its corresponding radical (R[•]).

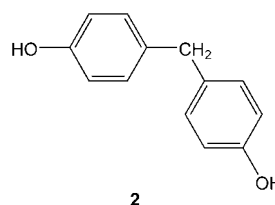


In a recent work, we have used time-resolved photoacoustic calorimetry (TR-PAC) to determine the C–H bond dissociation enthalpies of several alkylbenzenes (toluene, ethylbenzene, and cumene).^[5] To broaden our understanding of the substituent effects on the benzylic C–H bond, we decided to extend that study to a pair of substituted diphenylmethanes, specifically 4-hydroxydiphenylmethane (1) and bis(4-hydroxyphenyl)methane (2), aiming to in-



investigate the substituent effect of the *para*-hydroxyphenyl group(s) on the benzylic C–H bond dissociation enthalpy.

Based on thermodynamic data alone, we would expect that the hydrogen abstraction [reaction (2)] would take place primarily at the –CH₂– group. Using basic organic chemistry rules, one can expect the methylene C–H bond in the substituted diphenylmethanes to be weaker than in toluene, due to the combined resonance effect of the two adjoining aromatic groups.^[6] Indeed, the gas phase C–H bond dissociation enthalpy in toluene, $DH^{\circ}(\text{PhCH}_2\text{–H})$, is $375 \pm 5 \text{ kJ mol}^{-1}$,^[7] whereas in diphenylmethane it is $33\text{--}39 \text{ kJ mol}^{-1}$ lower.^[8–10] On the other hand, the O–H bond dissociation enthalpy in phenol, $DH^{\circ}(\text{PhO–H}) = 371.3 \text{ kJ mol}^{-1}$,^[1a] is only slightly lower than $DH^{\circ}(\text{PhCH}_2\text{–H})$, in line with the discussion by Ingold and Wright.^[11] Although the value for the O–H bond dissociation enthalpy is not available for the substituted diphenylmethanes, it could be expected to be similar to the value in *para*-methylphenol (363 kJ mol^{-1}),^[1a] that is, some 8 kJ mol^{-1} lower than $DH^{\circ}(\text{PhO–H})$.^[12] The C–H bond dissociation enthalpies in the title compounds are also unavailable, but they should be similar or even smaller than in diphenylmethane, due to the presence of the electron-donating *para*-OH groups.^[2a]



Results and Discussion

TR-PAC allows the independent determination of the enthalpies of reactions (1) and (2) presented above.^[5,13] The R–H bond dissociation enthalpy in solution, $DH_{\text{sln}}^{\circ}(\text{R–H})$, was derived from the enthalpy of reaction (2) ($\Delta_r H_2$), which is simply twice the difference between that quantity and the solution-phase O–H bond dissociation enthalpy of *tert*-butyl alcohol, Equation (4).

$$DH_{\text{sln}}^{\circ}(\text{R–H}) = \Delta_r H_2 / 2 + DH_{\text{sln}}^{\circ}(t\text{-BuO–H}) \quad (4)$$

In a previous work we have determined $DH_{\text{sln}}^{\circ}(t\text{-BuO–H}) = 462.7 \pm 3.5 \text{ kJ mol}^{-1}$ in acetonitrile,^[14] the solvent used in the experiments described herein. No assumptions have yet been made at this point regarding which bond is actually being broken in RH. The TR-PAC results for $DH_{\text{sln}}^{\circ}(\text{R–H})$ are displayed in Table 1.

To derive the related gas-phase values, $DH^{\circ}(\text{R–H})$, the solvation terms illustrated in Equation (5) must be considered.

$$DH^{\circ}(\text{R–H}) = DH_{\text{sln}}^{\circ}(\text{R–H}) + \Delta_{\text{sln}} H^{\circ}(\text{RH}, \text{g}) - \Delta_{\text{sln}} H^{\circ}(\text{R}^{\bullet}, \text{g}) - \Delta_{\text{sln}} H^{\circ}(\text{H}^{\bullet}, \text{g}) \quad (5)$$

The solvation of the hydrogen atom is estimated as $\Delta_{\text{sln}} H^{\circ}(\text{H}^{\bullet}, \text{g}) = 5 \pm 1 \text{ kJ mol}^{-1}$ for organic solvents.^[1a,15] However, the differential solvation of the radical and its precursor depend on which type of radical is being produced. Let us assume that a carbon-centered radical is formed. For these rad-

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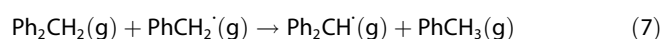
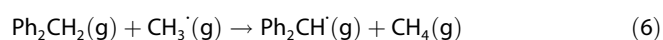
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Table 1. TR-PAC determination of solution bond dissociation enthalpies, DH_{sln}° of 4-hydroxydiphenylmethane and bis(4-hydroxyphenyl)methane.

Molecule	Concentration ^[a] [M]	$\Delta_{\text{obs}}H_2^{\circ}$ ^[b] [kJ mol ⁻¹]	$DH_{\text{sln}}^{\circ}(\text{R-H})$ [kJ mol ⁻¹]
(4-OHC ₆ H ₄)CH ₂ Ph	0.05	158.7 ± 4.2	373.5 ± 4.2
(4-OHC ₆ H ₄) ₂ CH ₂	0.01	154.7 ± 5.6	375.8 ± 4.7

[a] The substrate concentration was adjusted to obtain a rate of reaction (2) that would ensure a good temporal separation between the processes involved [reactions (1) and (2)] and thus increase the accuracy of the deconvolution method. [b] Measured enthalpic change for the sequential slower process, attributed to reaction (2) (see text). The values of $\Delta_{\text{obs}}H_2^{\circ}$ represent the average of five independent results and the uncertainties are twice the standard deviation of the mean.

icals there is evidence that $\Delta_{\text{sln}}H^{\circ}(\text{RH},\text{g}) \approx \Delta_{\text{sln}}H^{\circ}(\text{R},\text{g})$,^[5,16] so the difference between solution and gas-phase R–H bond dissociation enthalpies is equal to the solvation enthalpy of the hydrogen atom indicated above.^[17] Our TR-PAC solution results (Table 1) lead to $368.6 \pm 4.3 \text{ kJ mol}^{-1}$ and $370.8 \pm 4.8 \text{ kJ mol}^{-1}$ for the gas-phase R–H bond dissociation enthalpies in 4-hydroxydiphenylmethane and bis(4-hydroxyphenyl)methane, respectively. These results are only 5 kJ mol^{-1} lower than the recommended gas-phase PhCH₂–H bond dissociation enthalpy ($375 \pm 5 \text{ kJ mol}^{-1}$)^[7] and $26\text{--}34 \text{ kJ mol}^{-1}$ higher than the Ph₂CH–H bond dissociation enthalpy (see Introduction). The fact that we have obtained identical values for (the putative) C–H bond dissociation enthalpies in 4-hydroxydiphenylmethane and bis(4-hydroxyphenyl)methane would indicate that the influence of *para*-OH group is quite small. Therefore, one could expect that the above values were similar to $DH^{\circ}(\text{Ph}_2\text{CH-H})$. We tried to determine this bond dissociation enthalpy using TR-PAC, but the results were inconclusive, so we turned to computational chemistry for help. We have used density functional theory (DFT) to compute the enthalpy of isogyric and isodesmic reactions (6) and (7), from which $DH^{\circ}(\text{Ph}_2\text{CH-H})$ was derived as 345 kJ mol^{-1} , anchored in bond dissociation enthalpies of reference compounds.^[18] This value agrees well with the experimental value cited in ref. [9] ($342.3 \text{ kJ mol}^{-1}$).



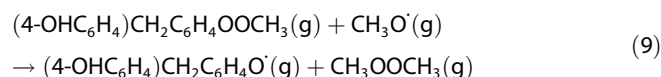
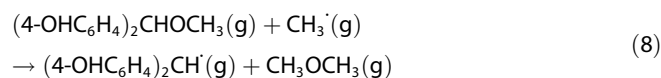
The above results and discussion seem to rule out that reaction (2) involves the cleavage of a sp^3 C–H bond from the title compounds and suggest that we were in fact measuring the O–H bond-dissociation enthalpy. In the absence of a flash-photolysis facility to confirm this conclusion, we decided to investigate this reaction by electron spin resonance (ESR) spectroscopy. For compound **2**, an ESR spectrum with hyperfine coupling constants from three pairs of equivalent hydrogens (1.68, 6.42, and 9.19 G) was observed. This hyperfine pattern is similar to the ones obtained for *para*-substituted phenoxy radicals,

like *para*-methylphenoxy ($2H_{2,6}=6.1$, $2H_{3,5}=1.4$, and $3H_{\alpha}=12.7 \text{ G}$)^[19] or the tyrosyl radical ($2H_{2,6}=6.2$, $2H_{3,5}=1.5$, and $2H_{\alpha}=15.0 \text{ G}$).^[20] The ESR spectrum was thus assigned to the 4-(4-hydroxyphenylmethyl)phenoxy radical, resulting from H-abstraction from the OH group. We note that the bis(4-hydroxyphenyl)methyl radical would have given a hyperfine pattern of two sets of four equivalent hydrogen atoms (phenyl groups) and one α hydrogen.

While the ESR experiment confirms that the product of reaction (2) is a phenoxy radical, it does not rule out the possibility of initial formation of a carbon-centered radical (recall that the TR-PAC and ESR methods involve quite different timescales, typically less than $1 \mu\text{s}$ and more than 1 ms , respectively). However, this possibility must be discarded on energetic grounds. According to the above thermochemical data, $DH_{\text{sln}}^{\circ}(\text{C-H}) \approx 350 \text{ kJ mol}^{-1}$ and $DH_{\text{sln}}^{\circ}(\text{O-H}) \approx 375 \text{ kJ mol}^{-1}$ (Table 1). Therefore, the hydrogen exchange reaction yielding the phenoxy radical from the carbon-centered radical in solution would be endothermic by some 25 kJ mol^{-1} (entropy effects must be negligible).

Why then is the least stable (phenoxy) radical formed in reaction (2)? This type of behavior, where the strongest bond is more prone to attack by a *tert*-butoxy radical, has been observed before for several amines.^[21] Tanko et al. have shown that, in this case, the activation entropy terms ($T\Delta^{\ddagger}S$) are more important than the enthalpy terms ($\Delta^{\ddagger}H$) and therefore determine the trend in the rate constants (the bulkiness of *t*-BuO[•] radical is related to this behavior). In our case, however, it is likely that the kinetic preference for the phenoxy radical is mainly due to the enthalpy barrier. Zavitsas and Chatgililoglu,^[22] using a model developed by the Zavitsas group, pointed out that although the C–H bond dissociation enthalpy in toluene and the O–H bond dissociation enthalpy in phenol are comparable (see Introduction), the activation enthalpy for the hydrogen abstraction reaction by a peroxy radical ROO[•] is much higher for the C–H bond. This is because the strength of the bond being broken is only a small part of the picture. According to their model, that bond strength actually represents the first of four terms needed to estimate the energy of the transition state. For discussing the kinetics of hydrogen abstraction from C–H in toluene versus O–H in phenol, the determining factor will be the difference between the bond dissociation enthalpies PhCH₂–OOR and PhO–OOR (the remaining terms are equal in both cases). These bond enthalpies reflect a triplet repulsion term in the transition states for hydrogen abstraction from C–H and O–H, respectively, which is responsible for raising the energy of those transition states. Since the bond dissociation enthalpy in PhO–OOR is at least 150 kJ mol^{-1} lower than in PhCH₂–OOR,^[22] the transition state for the O–H abstraction lies well below the transition state for the C–H abstraction. The relevant bond dissociation enthalpies in our reactions, for example, for compound **2**, are (4-OHC₆H₄)₂CH–OR and (4-OHC₆H₄)CH₂C₆H₄O–OR ($R=t\text{-Bu}$), and we have computed the enthalpies as 272 kJ mol^{-1} and 77 kJ mol^{-1} , respectively, from the enthalpies of model reactions (8) and (9) ($R=\text{CH}_3$), obtained from DFT calculations.^[23] The very low O–O bond dissociation enthalpy in the peroxide

must therefore be responsible for a low activation energy of the hydrogen abstraction from the O–H bond, as compared with the equivalent process involving the C–H bond [Eqs. (8) and (9)].



On the basis of all the above evidence, it seems clear that the product of reaction (2) is a phenoxy radical. We can now use the TR-PAC solution results to determine the gas-phase O–H bond dissociation enthalpies of 4-hydroxydiphenylmethane and bis(4-hydroxyphenyl)methane. In contrast to the case of carbon-centered radicals, the differential solvation energetics of phenols and their corresponding radicals are not negligible. However, we have recently shown that the problem can be avoided by deriving gas-phase values of the O–H bond dissociation enthalpies in substituted phenols, relative to the O–H bond dissociation enthalpy in phenol. When these relative values are obtained with Equation (10), the solvation terms [Equation (11)] nearly cancel out, implying that $\Delta DH^\circ(\text{ArO–H}) \approx \Delta DH^\circ_{\text{sln}}(\text{ArO–H})$.^[14]

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

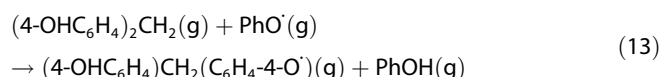
$$\Delta DH^\circ(\text{ArO–H}) = \Delta DH^\circ_{\text{sln}}(\text{ArO–H}) + [\Delta_{\text{sln}}H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{ArO}\cdot, \text{g})] - [\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}\cdot, \text{g})] \quad (11)$$

Another advantage of using relative values of O–H bond dissociation enthalpies is that they can be derived directly from the experimental enthalpies of reaction (2) for the substituted phenol ($\Delta_r H_2^\circ$) and for the phenol itself ($\Delta_r H_2^\circ$). This procedure [Equation (12)] avoids the uncertainties of auxiliary data. Using $\Delta_r H_2^\circ = -148.1 \pm 2.1 \text{ kJ mol}^{-1}$ from previous work,^[14] we obtained the results for $\Delta DH^\circ(\text{ArO–H})$ summarized in Table 2. These results can then be used together with $DH^\circ(\text{PhO–H}) =$

$371.3 \text{ kJ mol}^{-1}$ ^[1a] to calculate the absolute values of $DH^\circ(\text{ArO–H})$, also reported in Table 2.

$$\Delta DH^\circ(\text{ArO–H}) \approx \Delta DH^\circ_{\text{sln}}(\text{ArO–H}) = \Delta_r H_2^\circ / 2 - \Delta_r H_2^\circ / 2 \quad (12)$$

The values of $\Delta DH^\circ(\text{ArO–H})$ are only about 6 kJ mol^{-1} lower than our predictions based on the O–H bond dissociation enthalpy in 4-methylphenol (-8.3 kJ mol^{-1})^[1a] and on the Hammett plot (-9.4 kJ mol^{-1}).^[12] These predictions seem to be confirmed by DFT calculations for Equation (13), which yield $\Delta DH^\circ(\text{ArO–H}) = -7.7 \text{ kJ mol}^{-1}$.



To summarize, considering the uncertainties involved in the estimated, computed, and experimental results, the overall agreement is quite good and a single conclusion holds: although the sp^3 C–H bond from the title compounds is significantly weaker than the O–H bond (by 19 kJ mol^{-1} , if we believe the DFT results, or by approximately 13 kJ mol^{-1} , accepting the TR-PAC-based values) the hydrogen atom abstracted in reaction (2) belongs to the hydroxy group. Our study provides an interesting example of two competitive hydrogen-abstraction reactions involving the *same* molecule where the final product is determined by kinetics and not by thermodynamics. It also illustrates the usefulness of Zavitsas' model in understanding these observations.

Experimental Section and Computational Methods

Photoacoustic calorimetry: The instrumental setup and general experimental procedure is described in detail elsewhere.^[5,13] Briefly, argon-purged solutions in acetonitrile of di-*tert*-butylperoxide (ca. 0.4 M) and each substrate in the adequate concentration (see Table 1) were photolyzed in the calorimeter cell with a nitrogen laser. Deconvolution of the sound waves afforded the apparent enthalpic change, $\Delta_{\text{obs}}H$, related to the reaction enthalpies [see Eq. (1)] by $\Delta_r H = (E_m - \Delta_{\text{obs}}H) / \Phi_r + \Delta_r V / \chi$. Here, E_m represents the molar photon energy, Φ_r the reaction quantum yield, $\Delta_r V$ the reaction volume change, and χ the adiabatic expansion coefficient of the solvent. Only reaction (2) is of concern to us here, and its enthalpy is given by $\Delta_r H_2 = -\Delta_{\text{obs}}H_2 / \Phi_r$, assuming that the reaction volume change is negligible, that is $\Delta_r V_2 = 0$, and using 0.89 for the quantum yield of di-*tert*-butylperoxide homolysis in acetonitrile.^[24] Di-*tert*-butylperoxide was purified according to a literature procedure.^[25]

ESR spectroscopy: ESR experiments were done in acetonitrile containing *tert*-butyl peroxide (300 mM) and the hydroxy compound (3 mM). The solutions were deaerated by bubbling with argon and allowed to flow through a quartz flat cell placed in the ESR cavity. Radicals were generated by *in situ* photolysis, using an optically focused high pressure Hg-Xe 1000 W lamp. X-band ESR spectra were recorded with a Bruker ESP300E spectrometer.

Theoretical calculations: The DFT calculations have been performed with the Adamo and Barone's Becke style one parameter functional using a modified Perdew–Wang exchange^[26] and PW91 correlation (PW91).^[27] The geometries have been fully optimized with the Dun-

Table 2. Relative and absolute gas-phase O–H bond dissociation enthalpies for 4-hydroxydiphenylmethane and bis(4-hydroxyphenyl)methane. Data in kJ mol^{-1} .

Molecule	$-\Delta_r H_2^\circ$ ^[a]	$\Delta DH^\circ(\text{ArO–H})$ ^[b]	$DH^\circ(\text{ArO–H})$ ^[c]
$\text{C}_6\text{H}_5\text{OH}$	148.1 ± 2.1	0	371.3
$(4\text{-OHC}_6\text{H}_4)_2\text{CH}_2\text{Ph}$	178.3 ± 4.7	–15.1	356.2
$(4\text{-OHC}_6\text{H}_4)_2\text{CH}_2$	173.8 ± 6.3	–12.9	358.4

[a] Enthalpies of reaction (2) measured by TR-PAC. [b] Gas-phase O–H bond dissociation enthalpies relative to phenol. [c] Absolute gas-phase O–H bond dissociation enthalpies.

ning's correlation consistent valence double zeta basis set (cc-pVDZ).^[28] Vibrational frequency analysis at the same theoretical level (MPW1PW91/cc-pVDZ) was used to verify if stationary points were in fact minimum energy structures. These frequency calculations also provided values for the thermal correction to enthalpy. Final values for the energies (Table 3), including thermal correc-

Table 3. Total energies calculated at the MPW1PW91/aug-cc-pVDZ//MPW1PW91/cc-pVDZ. Data include zero-point energies and thermal corrections to 298 K.

Molecule	Energy [hartree] ^[a]
Ph ₂ CH ₂	-502.328478
Ph ₂ CH	-501.704244
CH ₄	-40.458831
CH ₃	-39.798609
PhCH ₃	-271.393422
PhCH ₂	-270.757383
PhOH	-307.324262
PhO	-306.691333
CH ₃ OH	-115.654261
CH ₃ O	-114.998330
CH ₃ OCH ₃	-154.918349
CH ₃ OOCH ₃	-230.040610
(4-C ₆ H ₄ OH) ₂ CH ₂	-652.755370
(4-C ₆ H ₄ OH) ₂ CH	-652.132415
(4-C ₆ H ₄ OH)(4-C ₆ H ₄ O)CH ₂	-652.125382
(4-C ₆ H ₄ OH)(4-C ₆ H ₄ OOMe)CH ₂	-767.1350868
(4-C ₆ H ₄ OH) ₂ CHOCH ₃	-767.222660

[a] 1 hartree corresponds to 2625.5 kJ mol⁻¹.

tions, were obtained from single-point energy calculations using the Dunning's correlation consistent valence double zeta basis set augmented with diffuse functions (aug-cc-pVDZ). Thus, reaction enthalpies at 298 K were calculated at the MPW1PW91/aug-cc-pVDZ//MPW1PW91/cc-pVDZ theoretical level. The DFT calculations were performed with the Gaussian 98 Program.^[29]

Acknowledgements

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Keywords: bond energies • computational chemistry • photoacoustic calorimetry • radicals • thermochemistry

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$162.1 \pm 4.1 \text{ kJ mol}^{-1}$. These values and the enthalpies of reactions (8) and (9) lead to the C–OCH₃ and O–OCH₃ bond dissociation enthalpies quoted in the text.

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