

Substituent effects on the O–H bond dissociation enthalpies in phenolic compounds: agreements and controversies*

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Abstract: The available experimental data on O–H bond dissociation enthalpies in phenolic compounds indicate that the ring substituent effects on the thermodynamic stability of that bond can be predicted by using a group additivity method. However, the reliability of the estimates is still affected by the uncertainties assigned to many of those experimental results and also by the scarce information on the solvation of phenoxy radicals.

INTRODUCTION

Molecular properties are often rationalized on the basis of ‘substituent effects’. The procedure is rather intuitive, because it is akin to our mental response whenever a ‘new’ molecule is met: we always try to relate it to a simpler species and then start replacing atoms by other atoms or by chemical groups, until the molecule is finally built in our mind. The same general approach is used when probing substituent effects on a given property: we simply compare the values of that property for two structurally similar molecules.

The choice of the *reference* molecule, although arbitrary, is usually obvious. For instance, if we wish to study the influence of alkyl substituents on the C–H bond length in alkanes, methane is a suitable anchor; when we plan to discuss the pK_a 's of a series of aromatic compounds XC_6H_4COOH , where X is any chemical group, then benzoic acid (X = H) will probably be our base model. In the present paper, we are concerned with substituent effects on the thermodynamic stability of the O–H bond in phenolic compounds, thus a convenient reference will be phenol (PhOH) itself.

One of the main incentives for investigating the energetics of the hydroxyl bond in phenolic compounds (ArOH) is to gain a better understanding of the factors that account for the anti-oxidant behavior of many of those compounds [1]. A weak O–H bond in ArOH will imply that reaction 1, which represents the scavenging of a peroxy radical (ROO \cdot), will be thermodynamically more favorable, therefore increasing the anti-oxidant efficiency of the compound.



The thermochemistry of the O–H bond in phenolic compounds has been addressed by several research groups, using a variety of experimental and computational methodologies. The results of such studies have been analyzed in a recent review [2], leading to a set of recommended values for O–H bond dissociation enthalpies, which allowed to test empirical and theoretical models to predict new data. The

*Lecture presented at the 15th International Conference on Chemical Thermodynamics, Porto, Portugal, 26 July–1 August 1998, pp. 1167–1306.

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purpose of the present paper is to provide a more detailed discussion of one of those methods, and also to provide some insights into a topic which deserves more attention in future studies: the solvation of phenoxy radicals.

THE O–H BOND DISSOCIATION ENTHALPY IN PHENOL

As shown in Fig. 1, there are over 20 values reported for the PhO–H bond dissociation enthalpy, in solution and in the gas phase, at 298 K [3–25]. The selected gas phase value, 371.3 ± 2.3 kJ/mol [2], is displayed as a solid line and corresponds to the average of some of the data displayed.

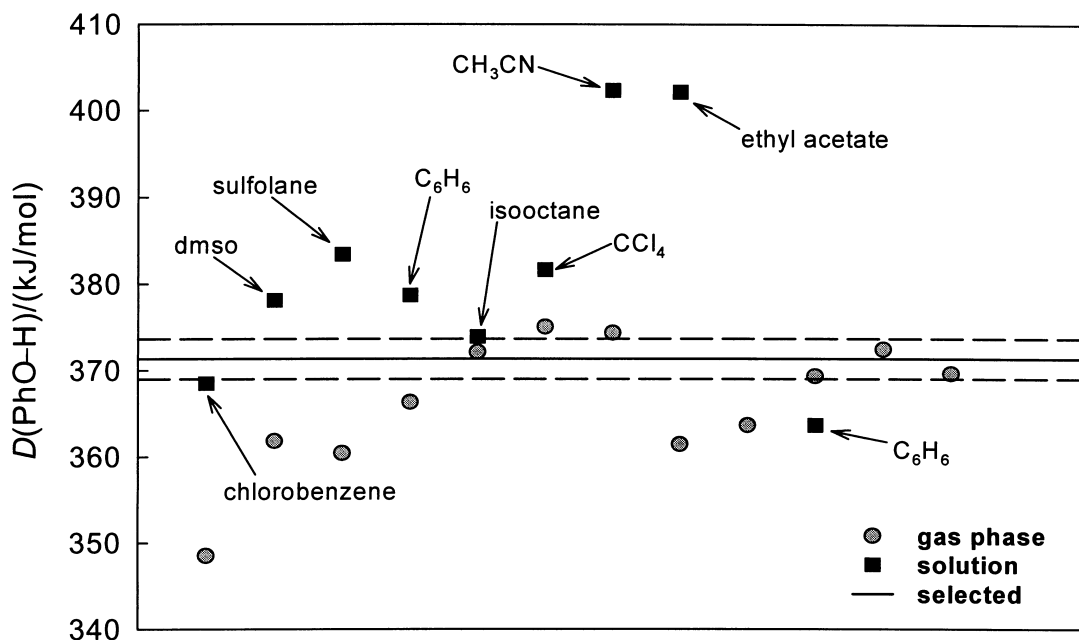


Fig. 1 Experimental data for the PhO–H bond dissociation enthalpy in solution and in the gas phase, at 298 K (values from [2]).

It is noted in Fig. 1 that, with the exception of two (probably less reliable) results, solution phase bond dissociation enthalpies, $D_{\text{sln}}(\text{PhO}-\text{H})$, are higher than 371.3 kJ/mol. To interpret this trend, let us consider the thermochemical cycle in Fig. 2, where $D(\text{PhO}-\text{H})$ is the gas phase bond dissociation enthalpy and $\Delta_{\text{sln}}H^\circ$ represent standard solution (or solvation) enthalpies. This scheme, or eqn 2, indicates that the enthalpy of solvation of the hydrogen atom and the difference between the enthalpies of solvation of phenol and the phenoxy radical are required to relate $D(\text{PhO}-\text{H})$ to $D_{\text{sln}}(\text{PhO}-\text{H})$.

$$D(\text{PhO}-\text{H}) = D_{\text{sln}}(\text{PhO}-\text{H}) + \Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{H}^\cdot, \text{g}) \quad (2)$$

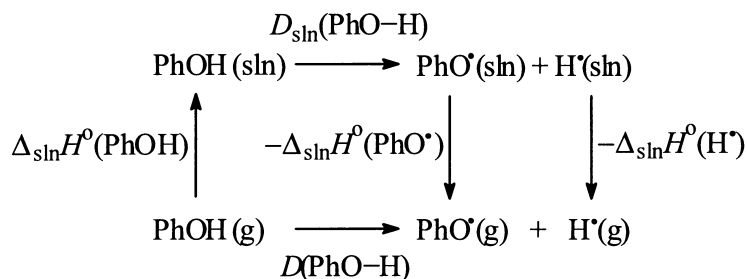


Fig. 2 Thermochemical cycle relating solution and gas phase PhO–H bond dissociation enthalpies.

The enthalpy of solvation of the hydrogen atom has never been experimentally determined. We can only estimate its value in a given solvent, based on some reasonable model. After a discussion by Parker [26] we have accepted that $\Delta_{\text{sln}}H^\circ(\text{H},\text{g}) \approx \Delta_{\text{sln}}H^\circ(\text{H}_2,\text{g})$ [2]. The solvation of the hydrogen molecule is endothermic in several common organic solvents ($\approx 5 \pm 1$ kJ/mol) and exothermic in water (≈ -4 kJ/mol). While the model may appear reasonable for many weakly polar organic solvents, it probably overestimates the solvation enthalpy of H in water, i.e. the true value is likely to be less than -4 kJ/mol. This is supported by AM1 (Austin Model 1) semiempirical calculations of the enthalpies of reactions 3 and 4, for clusters containing 2 to 7 molecules of water. The enthalpy of the former reaction is 3 kJ/mol ($n=2$) to 14 kJ/mol ($n=7$) more exothermic than the latter.



The differences between the enthalpies of solvation of phenol and the phenoxy radical in organic solvents have been discussed by Wayner *et al.* [23]. Solvents like isooctane and carbon tetrachloride, which are weak Lewis bases, will have negligible interactions both with PhOH and PhO $^\cdot$, so that $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) \approx 0$. On the other hand, strong Lewis base solvents like acetonitrile, ethyl acetate, dimethylsulfoxide, and sulfolane (tetramethylene sulfone), are also hydrogen bond acceptors, thus are able to form one hydrogen bond with PhOH. The enthalpy of this hydrogen bond will therefore be a good approximation of the difference $\Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g})$. The same conclusion can be drawn for weaker hydrogen bond acceptors like benzene and chlorobenzene.

Wayner *et al.* cite abundant literature data from which the enthalpies of hydrogen bonds between phenol and several solvents can be derived. For instance, the values for acetonitrile and for ethyl acetate are both 19.7 kJ/mol and for benzene is 4.2 kJ/mol [23]. While this method looks sensible, an alternative approach has been used in [2]. The so-called Electrostatic-Covalent model, also known as ECW model, developed by Drago and co-workers [27–29], is a more handy procedure to derive $\Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g})$. It relies on eqn 5, which 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 [27–29].

$$-\Delta H = E_A E_B + C_A C_B \quad (5)$$

Using the ECW model, the following values are obtained for $\Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g})$ (in kJ/mol): 0 (isooctane and carbon tetrachloride; estimated), -8.7 (benzene), -9 (chlorobenzene; estimated), -18.7 (acetonitrile), -19.8 (ethyl acetate), -29.4 (dimethylsulfoxide), and -29.4 (sulfolane; estimated). If these values are accepted, together with $\Delta_{\text{sln}}H^\circ(\text{H}^\cdot, \text{g}) = 5$ kJ/mol, then eqn 2 leads to the conclusion that most of the solution data in Fig. 1 yield gas phase bond dissociation enthalpies which are lower than the recommended $D(\text{PhO}-\text{H})$. The discrepancies are, however, fairly small for two of them: one of the values in benzene yields $D(\text{PhO}-\text{H}) = 365.0$ kJ/mol and the one in isooctane affords $D(\text{PhO}-\text{H}) = 368.9$ kJ/mol. It is noted, on the other hand, that the $D(\text{PhO}-\text{H})$ results derived from the $D_{\text{sln}}(\text{PhO}-\text{H})$ data in acetonitrile, ethyl acetate, and carbon tetrachloride, are only 5–7 kJ/mol higher than 371.3 kJ/mol. Considering the above approximations, the agreement is also acceptable. It remains to be said that all the ‘best’ solution data come from photoacoustic calorimetry (PAC) experiments [23,24] and that the average gas phase bond dissociation enthalpy derived from all these $D_{\text{sln}}(\text{PhO}-\text{H})$ PAC results is 373.3 ± 5.4 kJ/mol, quite close to 371.3 kJ/mol.

It would be both interesting and important to have a value for $D_{\text{sln}}(\text{PhO}-\text{H})$ in water. With that in mind, we have performed several photoacoustic calorimetry experiments, but the final result is still hindered by the lack of some auxiliary data [30]. Yet, it is possible to make an estimate of $D_{\text{sln}}(\text{PhO}-\text{H})$, based on the gas phase value recommended above and on the calculation of the difference $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g})$. The method for this calculation was again the AM1. The estimated enthalpies of reactions (6) and (7), where parentheses were used to indicate clusters, are -34.5 kJ/mol and -27.9 kJ/mol, respectively, suggesting that $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) \approx -7$ kJ/mol. Using $\Delta_{\text{sln}}H^\circ(\text{H}, \text{g})$

≈ -4 kJ/mol, we finally obtain $D_{\text{sln}}(\text{PhO}-\text{H}) \approx 374$ kJ/mol.



The value estimated for $D_{\text{sln}}(\text{PhO}-\text{H})$ in water is only ≈ 4 kJ/mol higher than the gas phase bond dissociation enthalpy. This appears to be at variance with the trend discussed above, where $D_{\text{sln}}(\text{PhO}-\text{H})$ is higher for solvents which are strong proton acceptors. While this is also predicted for water, as indicated by the enthalpy of reaction 6 (-34.5 kJ/mol), the AM1 calculations show that the interaction is also strong for the phenoxy radical. In other words, for the organic solvents mentioned, we have considered that $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g})$ is equal to the enthalpy of the hydrogen bond between phenol and the solvent molecule. In water, however, this approximation does not seem to hold because the phenoxy radical can act as an acceptor.

A relevant question is, of course, how reliable are these semiempirical molecular orbital calculations. Although it is recognized that the solvation of PhOH and PhO[·] deserves to be addressed with higher levels of theory (see below), it is fair to say that some simple tests performed with the AM1 hamiltonian led to sensible results. For instance, AM1 predicts a reasonable value [31] for the interaction of two water molecules (-22.9 kJ/mol) and yields 40.2 kJ/mol for ‘reaction’ (8), which is only 4 kJ/mol lower than the standard vaporization enthalpy of water at 298 K. Moreover, a value for the enthalpy of reaction 6 at 0 K (-38.6 kJ/mol), calculated at the Hartree–Fock level with a 6-31G(*d,p*) basis set [32], is in satisfactory agreement with the AM1 result mentioned above (-34.5 kJ/mol).



In order to obtain a better estimate $\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g})$, we have computed the enthalpy of reaction (9) at 0 K by using density functional (DFT) calculations for PhOH, PhO, and for the (PhOH·2H₂O) and (PhO[·]·2H₂O) clusters. Complete geometry optimizations with the Becke’s three-parameters hybrid functional [33] that includes a mixture of Hartree–Fock exchange with DFT exchange–correlation and which is represented by B3LYP have been carried out. The 6-31G** basis set has been used in all optimizations and zero point vibrational energies (ZPVE) at the same theoretical level (B3LYP/6-31G**) were also calculated. DFT ZPVE’s values were unscaled. We have also verified that theoretical calculations at this level (B3LYP/6-31G**) provides a very good description of the structure and dimerization energy of the water dimer.



A schematic view of the interactions of PhOH and PhO[·] with two water molecules is shown in Fig. 3, based on the B3LYP/6-31G** calculations. The cyclic structure involving phenol and the water molecules forms three strong hydrogen bonds. The computed distances O1–H2, O2–H3, and O3–H1 are 196, 184, and 176 pm, respectively (the O–H bond length in the water dimer, calculated at the same theory level, is 193.8 pm). In the case of the fenoxo radical, at the right hand side of Fig. 3, hydrogen bonds are observed between O1 and H2 (182 pm) and between O2 and H3 (179 pm), that is, only one water molecule is interacting with the radical. The energetics reflect these observations: reaction (9) at 0 K is 7.2 kJ/mol exothermic. Interestingly, this value matches the one obtained with the AM1 calculations.

THE O–H BOND DISSOCIATION ENTHALPIES IN SUBSTITUTED PHENOLS

Although the experimental information on the energetics of the O–H bond in substituted phenols (ArOH) is fairly abundant, only a few bond dissociation enthalpies refer to the gas phase—the vast majority of the data come from solution studies [2]. The relationship between $D(\text{ArO}-\text{H})$ and $D_{\text{sln}}(\text{ArO}-\text{H})$ is similar to eqn (2), i.e. it includes the term $\Delta_{\text{sln}}H^\circ(\text{ArOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{ArO}^\cdot, \text{g})$ and the enthalpy of solvation of the hydrogen atom. Unfortunately, our knowledge about the solvation thermodynamics of these phenolic species is even more scarce than in the case of phenol itself. Hence, in order to reach our goal—discussing substituent effects on ArO–H bond dissociation enthalpies—we must elude that problem by making some reasonable assumption. If eqn (2) is used together with a similar relation for ArOH, we can express the substituent effect on $D(\text{ArO}-\text{H})$ and $D_{\text{sln}}(\text{ArO}-\text{H})$ relative to the bond

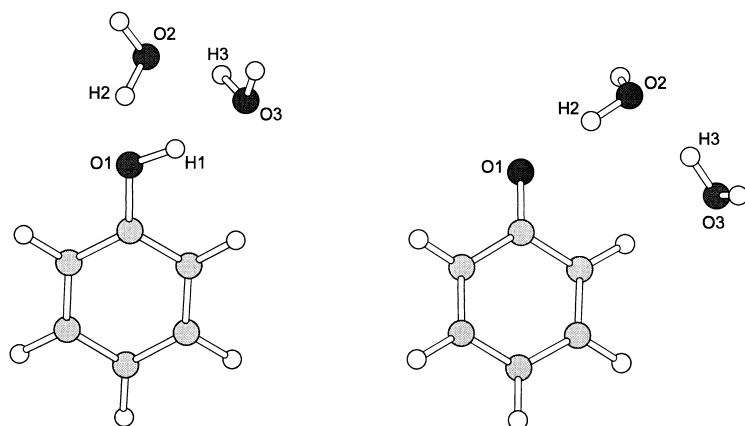


Fig. 3 Optimized geometries, at the B3LYP/6-31G** theory level, of (PhOH)2H2O and (PhO^o)2H2O clusters.

dissociation enthalpies in PhOH:

$$\Delta D(\text{O} - \text{H}) = D(\text{ArO} - \text{H}) - D(\text{PhO} - \text{H}) \quad (10)$$

$$\Delta D_{\text{sln}}(\text{O} - \text{H}) = D_{\text{sln}}(\text{ArO} - \text{H}) - D_{\text{sln}}(\text{PhO} - \text{H}) \quad (11)$$

$$\begin{aligned} \Delta D(\text{O} - \text{H}) = \Delta D_{\text{sln}}(\text{O} - \text{H}) + [\Delta_{\text{sln}}H^\circ(\text{PhOH}, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{ArOH}, \text{g})] - [\Delta_{\text{sln}}H^\circ(\text{PhO}^\cdot, \text{g}) \\ - \Delta_{\text{sln}}H^\circ(\text{ArO}^\cdot, \text{g})] \end{aligned} \quad (12)$$

The required assumption is now obvious: we will consider that the two bracketed terms in eqn (12) will cancel, so that the relation $\Delta D(\text{O} - \text{H}) \approx \Delta D_{\text{sln}}(\text{O} - \text{H})$ holds for any solvent. The reliability of this approximation is open to speculation, but we believe it will not be worse than the typical experimental uncertainties in the O–H bond dissociation enthalpies ($\approx 4\text{--}8$ kJ/mol).

The use of a relative scale of $D(\text{O} - \text{H})$ brings two additional advantages. First the (somewhat uncertain) enthalpy of solvation of the hydrogen atom cancels out. Second, eqn (12) avoids the systematic errors that may affect the experimental values of the bond dissociation enthalpies. It is not uncommon to find significant disagreements between the values of $D(\text{ArO} - \text{H})$ or $D_{\text{sln}}(\text{ArO} - \text{H})$, determined through different laboratory techniques or reported by different research groups [2]. In many of these cases, the discrepancies are simply due to different auxiliary data (namely, different values accepted for the O–H bond dissociation enthalpy in a given reference compound). When the relative data are considered, the inconsistency is removed and a much better agreement is obtained.

A list of selected group contributions to $\Delta D(\text{O} - \text{H})$ is presented in Table 1 (data from [2] those in parentheses are estimates). The values in the second column represent the contribution of a single substituent in the aromatic ring; those in the fourth column refer to the effect of a second substituent on $\Delta D(\text{O} - \text{H})$. For example, when one hydrogen at the *ortho* position in phenol is replaced by a methyl group, the O–H bond dissociation enthalpy decreases by 9 kJ/mol; the replacement of the second *ortho* hydrogen leads to a further 5 kJ/mol weakening of the O–H bond. In other words, the O–H bond dissociation enthalpy in 2,6-dimethylphenol is -14 kJ/mol lower than in phenol.

The second column of Table 1 contains but a sample of the available group contributions to $\Delta D(\text{O} - \text{H})$ in monosubstituted phenols (additional data, based on experimental work or estimated from linear correlations between $\Delta D(\text{O} - \text{H})$ and Hammett parameters, are available in [2]). Yet, the information presented here is sufficient to show that, although a considerable number of group contributions in monosubstituted phenols is known, some data are affected by uncertainties comparable to the $\Delta D(\text{O} - \text{H})$ values themselves. Therefore, even conceding that some of the error bars in Table 1 are slightly overestimated, they may obscure the fine detail of a discussion on substituent effects.

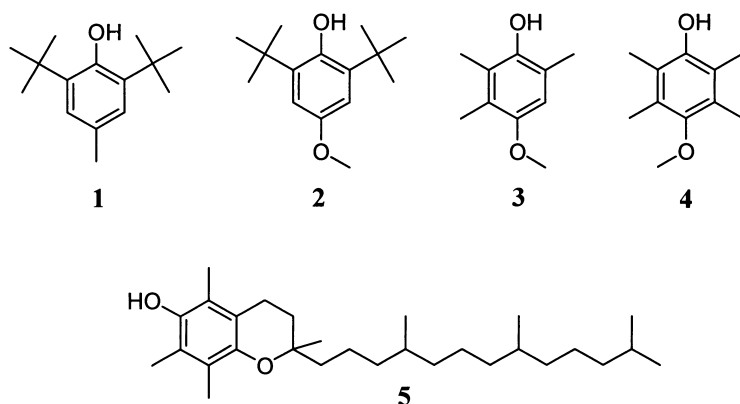
The accuracy and the precision of group contributions to $\Delta D(\text{O} - \text{H})$ becomes of course more important when we want to predict the effect of several ring substituents. The values in the fourth column, which, as stated above, represent the effect of the *second* substituent, were obtained from the differences

Table 1 Some substituent contributions to the changes in the O–H bond dissociation enthalpy of phenol ($T = 298$ K). Data in kJ/mol

First substituent	$\Delta D(\text{O-H})$	Second substituent	$\Delta D(\text{O-H})$
2-Me	-9 ± 4	6-Me	-5 ± 6
3-Me	-3 ± 4	5-Me	0 ± 6
4-Me	-8 ± 4		
2- <i>t</i> -Bu	(-15)	6- <i>t</i> -Bu	-11
3- <i>t</i> -Bu	(-5)	5- <i>t</i> -Bu	-1
4- <i>t</i> -Bu	-7 ± 4	2- <i>t</i> -Bu	-15 ± 9
2-OH	-30 ± 8		
3-OH	1 ± 8		
4-OH	-27 ± 10		
2-OMe	-17 ± 4	6-OMe	-4 ± 9
3-OMe	0 ± 4	5-OMe	-7 ± 9
4-OMe	-22 ± 4		
2-CN	0 ± 8		
3-CN	13 ± 8		
4-CN	18 ± 8		
2-NO ₂	$> -5 \pm 8$	6-NO ₂	< 31
3-NO ₂	19 ± 8		
4-NO ₂	$< 25 \pm 8$		
2-Cl	-3 ± 4	6-Cl	2 ± 9
3-Cl	5 ± 4	5-Cl	9 ± 6
4-Cl	-1 ± 4		

between the experimental $\Delta D(\text{O-H})$ values for disubstituted and monosubstituted phenols. Naturally, the error bars are larger than those in the second column. The main question is therefore if the data in Table 1 can be used to predict reliable $\Delta D(\text{O-H})$ values for polysubstituted phenols.

Let us consider two important artificial anti-oxidants in food [34], known as BHT (butylated hydroxytoluene or 2,6-*tert*-butyl-4-methylphenol, **1**) and BHA (butylated hydroxyanisole or 2,6-*tert*-butyl-4-methoxyphenol, **2**). The selected experimental (Reinsert) for these molecules are -32 ± 8 kJ/mol and -45 ± 4 kJ/mol, respectively [2]. It is noted that both are accurately estimated from the data in Table 1: the calculated values are $(-15-11-8) = -34$ kJ/mol for BHA and $(-15-11-22) = -48$ kJ/mol for BHT.



A good agreement is also observed between the experimental and the calculated (Reinsert) values for 2,3,6-trimethyl-4-methoxyphenol (**3**), -38 ± 8 kJ/mol and $(-9-5-3-22) = -39$ kJ/mol. However, when another methyl group is introduced at the *meta* position, yielding the compound 4-methoxytetramethylphenol [4], a 12-kJ/mol discrepancy is found between the experimental (-27 ± 8 kJ/mol)

and the calculated (-39 kJ/mol) $\Delta D(\text{O}-\text{H})$ values. Although this difference is almost covered by the net uncertainty ($\approx \pm 11$ kJ/mol) of the group contribution result, there is a likely alternative explanation, suggested by Ingold and co-workers [35,36], Due to a steric interaction with the two *meta*-methyl substituents, the methoxy group is forced out of the aromatic plane, therefore decreasing the stabilizing conjugation between the oxygen and the aromatic ring. The phenoxy radical is thus less stabilized than predicted by the data in Table 1. This idea is in keeping with the experimental value for the $\Delta D(\text{O}-\text{H})$ in α -tocopherol (or vitamin E, **5**), where the more rigid structure of the chromanol ring forces the O-C(sp²) bond to be more planar with the ring [35]. This $\Delta D(\text{O}-\text{H})$ value, -43 ± 4 kJ/mol, is very close to the group contribution result obtained for **4**.

The above examples indicate that a judicious use of the group contribution method may afford fairly reliable $\Delta D(\text{O}-\text{H})$ data and provide important insights into the factors that affect the stability of the O–H bond in phenolic compounds. However, they also show that efforts to reduce the uncertainties in experimental data are badly required.

ACKNOWLEDGEMENTS

The financial support provided by the PRAXIS XXI Programme, Portugal (PRAXIS/2/2.1/QUI/51/94), is gratefully acknowledged.

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