Energetics of the O–H Bond in Phenol and Substituted Phenols: A Critical Evaluation of Literature Data

Rui M. Borges dos Santos

Unidade de Ciências e Tecnologias Agrárias and CiTecMat, Universidade do Algarve, Campus de Gambelas, 8000 Faro, Portugal

José A. Martinho Simões[a)]

Departamento de Química e Bioquímica and CiTecMat, Faculdade de Ciências, Universidade de Lisboa, 1700 Lisboa, Portugal

Received December 8, 1997; revised manuscript received March 24, 1998

This review presents a critical assessment of the available experimental information (contained in ~90 literature references) on the thermochemistry of the O–H bond in phenol and substituted phenols. The analysis led to a set of recommended values for the O–H bond dissociation enthalpies, which in turn allowed us to discuss several empirical and theoretical methodologies used to estimate these data. © *1998 American Institute of Physics and American Chemical Society.* [S0047-2689(98)00303-1]

Key words: bond dissociation enthalpy; energetics; phenol; phenolic compounds; substituent effects; substituted phenols; thermochemistry.

Contents

List of Tables

List of Figures

a)Author to whom correspondence should be addressed.

1. Introduction

Phenolic compounds play a major role in the chemistry of living organisms and life-supporting substances. The enormous interest in their antioxidant activity *in vitro* and *in vivo* is demonstrated by a wealth of research in recent years and also by frequent reports in the popular literature.[1] Aging, food, and wine, are indeed three topics which stimulate everybody's interest.

The properties of the O–H bond appear to be essential to understanding the chemical and biochemical behavior of phenolic compounds, for this is the bond that must be broken to generate the truly active species: the phenoxy radicals. It is thus not surprising that a large number of current studies, using a diversity of modern experimental and computational tools, have been addressing the kinetic and the thermodynamic stabilities of the phenolic bond and how these stabilities are affected by the number, nature, and position of the substituents in the aromatic ring. Despite all the efforts, the present knowledge on the energetics of the phenolic bond is still unsatisfactory. Even for the simplest of those molecules—phenol itself—the published values for the O–H bond dissociation enthalpy vary in a wide range (although a fairly precise number can be selected).

The present review aims: (1) to bring together all the available experimental data for the thermochemistry of the phenolic O–H bond, (2) to provide a selection of the "best" values, (3) to use these values to assess our understanding of the substituent effects, and (4) to test some empirical and theoretical methodologies which have been applied to estimate those O–H bond dissociation enthalpies not experimentally determined. Being a critical survey, this exercise led to some changes in the literature data. It was gratifying to find that, in some cases, the discrepancies in the results obtained by different groups are not as bad as originally claimed; in other—fortunately less frequent—instances, the disagreement increases.

Although we have tried to be comprehensive (the literature has been covered through the end of 1997), we felt it was unnecessary to include all the results which have only historical interest. This is the case, for example, for values derived from standard electron-impact mass spectrometry studies. Another point that should be stressed here is related to the auxiliary data used. In any work where experimental results are compared or used to recalculate values, it is essential to keep in mind the "thermodynamic consistency" of data—an issue which is sometimes forgotten in literature reports. As the present survey is centered on the stability of the O–H bond, no attempt has been made to examine the data for the enthalpies of formation of the parent phenols[2,3] and other species like alkyl radicals.[4] These data, which are thought to be reliable and internally consistent, are collected in the Appendix.

2. The PhO–H Bond Dissociation Enthalpy: Gas Phase Studies

One of the first literature values for the gas phase O–H bond dissociation enthalpy in phenol, D(PhO–H) $=368$ kJ mol^{-1} (Ph=phenyl) was reported by Benson in 1965.[5] The origin of this number is not clear, but it may be an estimate based on appearance energy measurements using electron-impact mass spectrometry. Fine and Westmore,[6] and also Laye and co-workers,[7] accepted that value and adopted 54 ± 21 kJ mol^{-1} for the enthalpy of the formation of the phenoxy radical, PhO$^{\bullet}$.

In 1975, Paul and Back used a toluene scavenging technique to determine the Arrhenius parameters of reaction 1 (Me=methyl) in the temperature range of 720–795 K:[8]

$$\mathrm{PhOMe(g)} \rightarrow \mathrm{PhO^{\bullet}(g)} + \mathrm{Me^{\bullet}(g)}. \qquad (1)$$

The activation energy, 242.7 ± 8.4 kJ mol^{-1}, was identified with the reaction enthalpy at 758 K, by assuming that the radical recombination [reverse of reaction (1)] has zero activation energy. The estimated correction to room temperature, -3.8 kJ mol^{-1}, led to $\Delta_r H^\circ(1)=238.9$ kJ mol^{-1} at 298 K.[8]

According to subsequent studies (see below), it is probably more correct to consider that the temperature adjustment to 298 K is negligible. On the other hand, for a unimolecular gas phase reaction, the enthalpy of reaction ($\Delta_r H^\circ$) is related to the difference between the forward and reverse activation energies (ΔE_a) by

$$\Delta_r H^\circ(T) = \Delta E_a(T) + RT. \qquad (2)$$

Therefore, the enthalpy of reaction (1) at 298 K, under the assumption of a negligible activation barrier for radical recombination, is derived as 249.0 ± 8.4 kJ mol^{-1}. The auxiliary data in the Appendix enabled the calculation of the enthalpy of formation of the phenoxy radical and the O–H bond dissociation enthalpy in phenol as 34.1 ± 8.5 and 348.5 ± 8.5 kJ mol^{-1}, respectively.

More recently, Mackie, Doolan, and Nelson have also investigated the unimolecular decomposition of anisole [reaction (1)], in the temperature range of 850–1000 K, by using a stirred reactor.[9] The obtained activation energy, 267.8±2.5 kJ mol^{-1}, can be handled as described above, leading to (T=298 K) $\Delta_r H^\circ(1)$=275.5±2.5 kJ mol^{-1}, $\Delta_f H^\circ_m$(PhO$^\bullet$,g) =60.6±2.8 kJ mol^{-1}, and D(PhO–H)=375.0±2.9 kJ mol^{-1}.

The rate constants reported in the two previous publications[8,9] were combined by Back,[10] affording an activation energy of 255.2±8.4 kJ mol^{-1} at 800 K, and implying a reaction enthalpy of 261.9±8.4 kJ mol^{-1} at 298 K. The resulting values for the enthalpy of formation of PhO$^\bullet$ and D(PhO–H) are calculated as 47.0±8.5 and 361.4±8.5 kJ mol^{-1}, respectively.

Colussi, Zabel, and Benson, in 1977, used the very low pressure pyrolysis (VLPP) method to probe the thermal decomposition kinetics of phenyl ethyl ether (PhOEt) and phenyl allyl ether ($PhOC_3H_5$), according to reactions (3) and (4):[11]

$$PhOEt(g) \rightarrow PhO^\bullet(g) + Et^\bullet(g), \quad (3)$$

$$PhOC_3H_5(g) \rightarrow PhO^\bullet(g) + C_3H_5^\bullet(g). \quad (4)$$

The high pressure activation energies of these reactions were derived by using the Rice–Ramsperger–Kassel (RRK) model and therefore rely on estimated A factors. Assuming that the activation energies of the reverse processes are negligible, the authors obtained 267.8 and 211.7 kJ mol^{-1}, respectively, for the enthalpies of reactions (3) and (4) at 298 K.[11] These values, together with the selected auxiliary data in the Appendix, yield $\Delta_f H^\circ_m$(PhO$^\bullet$,g)=47.2 kJ mol^{-1} [reaction (3)] and 47.6 kJ mol^{-1} [reaction (4)]. Interestingly, these results are in much better agreement than those derived in the original paper (51.0 and 43.9 kJ mol^{-1}, respectively). The discrepancies are, of course, due to the use of different auxiliary data. While the enthalpy of formation of gaseous phenyl ethyl ether is well established,[2] no experimental value is available for $\Delta_f H^\circ_m(PhOC_3H_5,g)$. The estimate[12] selected in the Appendix is presumably more reliable than either the one quoted in the paper by Colussi, Zabel, and Benson (2.1 kJ mol^{-1}) or the value calculated from the NIST STRUCTURES AND PROPERTIES program (−2.6 kJ mol^{-1}).[13]

The average enthalpy of formation of the phenoxy radical from the above VLPP studies, 47.4±8.0 kJ mol^{-1}, together with auxiliary data in the Appendix, lead to 361.8 ±8.1 kJ mol^{-1} for the PhO–H bond dissociation enthalpy. The uncertainty assigned to $\Delta_f H^\circ_m$(PhO$^\bullet$,g) is an estimate.

Shock tube experiments by Lin and Lin[14] on the unimolecular decomposition of anisole [reaction (1)] were analyzed by Tsang[4] and led to 57.7±8 kJ mol^{-1} for the enthalpy of formation of the phenoxy radical. The PhO–H bond dissociation enthalpy consistent with this value is 372.1±8 kJ mol^{-1}.

Suryan, Kafafi, and Stein used the VLPP method, together with Rice–Ramsperger–Kassel–Marcus (RRKM) calculations, to derive the high pressure limits of the activation parameters of reaction (1), and obtained E_a=265.7 kJ mol^{-1} at $T\approx$1100 K.[15] Using the methodology and assumptions described above, this result leads to (T=298 K) $\Delta_r H^\circ(1)$=274.8 kJ mol^{-1}, $\Delta_f H^\circ_m$(PhO$^\bullet$,g)=59.9 kJ mol^{-1}, and D(PhO–H)=374.3 kJ mol^{-1}. Tsang's assessment[4] of the same data yielded $\Delta_f H^\circ_m$(PhO$^\bullet$,g)=47.7±8 kJ mol^{-1}, which implies D(PhO–H)=362.1±8.1 kJ mol^{-1}.

The kinetics of the thermal decompositions of PhOEt [reaction (3)] and PhOBu [reaction (5); Bu=butyl] have been probed by Walker and Tsang, in 1990, through the single-pulse shock tube technique.[16]

$$PhOBu(g) \rightarrow PhO^\bullet(g) + Bu^\bullet(g). \quad (5)$$

The obtained activation energies, 268.5 kJ mol^{-1} (PhOEt; mean temperature 1050 K) and 274.4 kJ mol^{-1} (PhOBu; mean temperature 1030 K), together with Eq. (2) and the assumption of negligible activation barriers for radical recombination, lead to $\Delta_r H^\circ(3)$=277.2 kJ mol^{-1} (T=1050 K) and $\Delta_r H^\circ(5)$=283.0 kJ mol^{-1} (T=1030 K). The corrections to 298 K can be made in both cases by using $\Delta_r C^\circ_p$=9.83 J mol^{-1} K^{-1} estimated by Coloussi, Zabel, and Benson[11] for reaction (3). One obtains (T=298 K) $\Delta_r H^\circ(3)$=269.8 kJ mol^{-1} and $\Delta_r H^\circ(5)$=275.8 kJ mol^{-1}. Values for the enthalpy of formation of the phenoxy radical are then derived as 49.2 and 54.9 kJ mol^{-1}, respectively, by using the auxiliary data in the Appendix. The resulting PhO–H bond dissociation enthalpies are 363.6 and 369.3 kJ mol^{-1}, respectively.

The most recent gas-phase kinetic studies, leading to the enthalpy of formation of phenoxy radical, were reported by Arends, Louw, and Mulder.[17] Using a tubular flow reactor, these authors investigated the kinetics of reaction (1) in the temperature range of 793–873 K and arrived at 266.1±2.9 kJ mol^{-1} for the activation energy at 823 K. As described above for the same reaction, Eq. (2) and the assumption of a zero activation barrier for radical recombination lead to (T=298 K) $\Delta_r H^\circ(1)$=272.9 kJ mol^{-1} [$\Delta_r C^\circ_p \approx 0$]. This value and the auxiliary data in the Appendix afford $\Delta_f H^\circ_m$(PhO$^\bullet$,g)=58.0 kJ mol^{-1} and D(PhO–H)=372.4 kJ mol^{-1}.

Using ion-cyclotron resonance mass spectrometry (ICR), DeFrees, McIver, and Hehre[18] measured the proton affinity (PA) of the phenoxy radical by double resonance bracketing techniques and obtained PA(PhO$^\bullet$,g)=855.2±8.4 kJ mol^{-1}. However, this value is anchored at 857.7 kJ mol^{-1} for the proton affinity of ammonia. The presently accepted value PA(NH_3,g)=854.0 kJ mol^{-1} [3(a)] yields PA(PhO$^\bullet$,g) =851.5±8.4 kJ mol^{-1}. The proton affinity can be related to D(PhO–H) by

$$D(PhO–H) = PA(PhO^\bullet) + IE(PhOH) - IE(H), \quad (6)$$

where IE(PhOH)=820.9±0.1 kJ mol^{-1} and IE(H)=1312.0 kJ mol^{-1} are adiabatic ionization energies.[3(b)] These auxiliary data lead to D(PhO–H)=360.4±8.4 kJ mol^{-1} and $\Delta_f H^\circ_m$(PhO$^\bullet$,g)=46.0±8.4 kJ mol^{-1}. It must be stressed

that, although Eq. (6) is an approximation, since the ionization energies refer to 0 K, the error is much smaller than the uncertainty assigned to the proton affinity.

The proton affinity of the phenoxy radical has also been determined by another type of mass spectrometry-based methodology, known as the "kinetic method." [19] The value obtained, 860.2 ± 1.3 kJ mol^{-1}, is consistent with PA(NH_3,g)=853.5 kJ mol^{-1},[20] rather close to the recommended PA(NH_3,g)=854.0 kJ mol^{-1} [3(a)] cited above. The small correction yields PA(PhO$^{\bullet}$,g)=860.7 ± 1.3 kJ mol^{-1}, which, together with Eq. (6) and the ionization energy data mentioned, gives D(PhO–H)=369.6 ± 8 kJ mol^{-1} and $\Delta_f H^{\circ}_m$(PhO$^{\bullet}$,g)=55.2 ± 8 kJ mol^{-1}. The uncertainties are estimates.

The gas-phase acidity of phenol, i.e., the Gibbs energy of reaction (7), has been determined from ion–molecule reaction equilibria experiments by several groups.[21–23] The most recent result, 1432.2 ± 8 kJ mol^{-1},[23] recommended in a compilation by Lias *et al.*,[24] together with the value for the reaction entropy, 96.2 ± 4 J mol^{-1} K^{-1},[24] leads to 1460.9 ± 8 kJ mol^{-1} for the reaction enthalpy, $\Delta_{acid}H$, which is related to D(PhO–H) by Eq. (8):

$$\mathrm{PhOH(g)\rightarrow PhO^-(g)+H^+(g)}, \tag{7}$$

$$D(\mathrm{PhO-H})=\Delta_{acid}H+\mathrm{EA(PhO^{\bullet})}-\mathrm{IE(H)}. \tag{8}$$

The adiabatic electron affinity of phenoxy radical, EA(PhO$^{\bullet}$), has been measured by Lineberger's group as 217.4 ± 0.6 kJ mol^{-1} [25] and the ionization energy of the hydrogen atom was given above [note that Eq. (8) is an approximation since the electron affinity and the ionization energy refer to 0 K]. The final results are D(PhO–H)=366.3 ± 8 kJ mol^{-1} and $\Delta_f H^{\circ}_m$(PhO$^{\bullet}$,g)=51.9 ± 8 kJ mol^{-1}.

There are several appearance energy measurements of $C_6H_5O^+$ ions listed in the *NIST Chemistry WebBook*,[3] involving a variety of precursors. Assuming that those species have the phenoxy cation structure, it is possible to use the data to estimate the enthalpy of formation of PhO$^{\bullet}$. The discussion shall be limited to the appearance energies measured by PIPECO and photoionization mass spectrometry methods, which are far more reliable than the electron impact-based results.

The appearance energy (AE) of PhO^+, using nitrobenzene as a precursor [reaction (9)], ranges from 10.89 ± 0.04 to 11.12 ± 0.05 eV.[3] If the average, 11.01 ± 0.1 eV, is accepted, the enthalpy of reaction (10) can be calculated as 236.4 ± 9.8 kJ mol^{-1} by the difference between AE(PhO^+) and IE(PhO$^{\bullet}$)=8.56 ± 0.02 eV.[3] This result refers to 0 K, but the correction to 298 K is small, ~2 kJ mol^{-1} [26]

$$\mathrm{PhNO_2(g)\rightarrow PhO^-(g)+NO(g)}, \tag{9}$$

$$\mathrm{PhNO_2(g)\rightarrow PhO^{\bullet}(g)+NO(g)}. \tag{10}$$

Using 238 ± 10 kJ mol^{-1} for the reaction enthalpy at 298 K, together with auxiliary data in the Appendix, one obtains 214 kJ mol^{-1} for the enthalpy of formation of the phenoxy radical. This value is clearly too high and demonstrates that the $C_6H_5O^+$ ion formed from $PhNO_2$ does not have the structure of PhO^+.

Anisole is the other precursor which has been used to measure the appearance energy of $C_6H_5O^+$ [reaction (11)]. The average of the two values listed in the *NIST Chemistry WebBook*[3] is 11.8 ± 0.1 eV

$$\mathrm{PhOMe(g)\rightarrow PhO^+(g)+Me^{\bullet}(g)}, \tag{11}$$

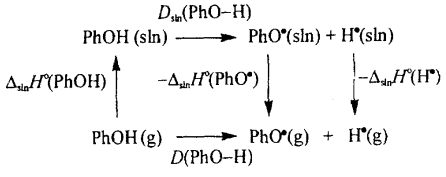
$$\mathrm{PhOMe(g)\rightarrow PhO^{\bullet}(g)+Me^{\bullet}(g)}. \tag{12}$$

Using the procedure described for nitrobenzene, the enthalpy of reaction (12) at 298 K is obtained as 316 ± 10 kJ mol^{-1} and the enthalpy of formation of the phenoxy radical as 101 kJ mol^{-1}. This value is almost in the range expected for $\Delta_f H^{\circ}_m$(PhO$^{\bullet}$,g). It suggests that in the experiments involving anisole, the phenoxy cation is indeed formed, but it may be produced with a considerable amount (~40 kJ mol^{-1}) of excess energy.

3. The PhO–H Bond Dissociation Enthalpy: Solution Studies

The energetics of the PhO–H bond has been investigated by several solution techniques. The data obtained can be compared with the gas phase values, under some simplifying assumptions. Although these assumptions often depend on the experimental method (see below), the general situation is displayed in Scheme 1. Here, D(PhO–H) and D_{sln}(PhO–H) represent the bond dissociation enthalpy in the gas phase and in solution, respectively, and $\Delta_{sln}H^{\circ}$ are solution (or solvation) enthalpies

$$\begin{aligned} D(\mathrm{PhO-H}) = {} & D_{sln}(\mathrm{PhO-H}) \\ & + \Delta_{sln}H^{\circ}(\mathrm{PhOH,g}) - \Delta_{sln}H^{\circ}(\mathrm{PhO^{\bullet},g}) \\ & - \Delta_{sln}H^{\circ}(\mathrm{H^{\bullet},g}), \end{aligned} \tag{13}$$



Scheme 1

Scheme 1, or Eq. (13), show that the calculation of the gas phase bond dissociation enthalpy requires the difference between the solvation enthalpies of the phenol and phenoxy radical, as well as the solvation enthalpy of the hydrogen atom in the solvent where the solution studies were performed.

When Scheme 1 refers to any species RH, R being, for instance, an alkyl radical, there is experimental evidence that the assumption $\Delta_{sln}H^{\circ}(\mathrm{RH})\approx\Delta_{sln}H^{\circ}(\mathrm{R^{\bullet}})$ is reliable, both in polar and in nonpolar solvents.[27] However, as discussed by Wayner *et al.*,[28] this is not true for R=PhO$^{\bullet}$ and solvents

TABLE 1. Some literature data for the solvation energetics of H_2. $T=298$ K

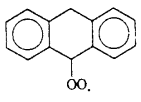
Solvent	$\Delta_{sln}H/(kJ\ mol^{-1})$	$\Delta_{sln}S/(J\ mol^{-1}\ K^{-1})$	Ref.
water	−4.1	−106.6	111
	−4.0	−106.4	113
hexane	5.1	−44.1	112
octane	4.0	−47.0	112
isooctane	3.7	−46.9	112
cyclohexane	5.2	−47.4	112
benzene	6.4	−47.4	112
toluene	5.1	−49.9	112
chlorobenzene	5.0	−51.9	112
acetone	4.5	−52.3	112
ethanol	3.7	−58.0	112
carbon tetrachloride	5.6	−47.7	112

which are strong Lewis bases, thus having the ability of forming hydrogen bonds to phenol. This topic will be discussed further.

The remaining term in Eq. (13) is the enthalpy of solvation of the hydrogen atom. This quantity is not experimentally available, but can be estimated by using a suitable model. After a detailed evaluation by Parker,[29] the following approximations will be accepted here: $\Delta_{sln}G^{\circ}(H^{\bullet},g) \approx \Delta_{sln}G^{\circ}(H_2,g)$ and $\Delta_{sln}H^{\circ}(H^{\bullet},g) \approx \Delta_{sln}H^{\circ}(H_2,g)$. Some selected data for the solvation energetics of the hydrogen molecule are listed in Table 1. It is noted that, in organic solvents, $\Delta_{sln}H^{\circ}(H_2,g)$ varies in a narrow range, with an average of $\sim 5 \pm 1$ kJ mol^{-1}. This value will be adopted in the present paper.

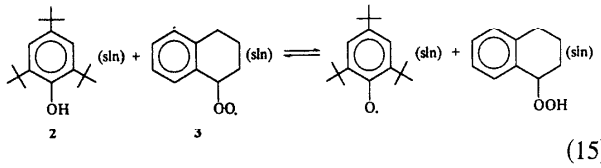
The kinetics and thermochemistry of phenol-inhibited oxidation of 9,10-dihydroanthracene has been investigated by Mahoney and DaRooge, in 1975.[30] Direct measurements of some of the rate constants involved in the mechanism, together with a computer fit of kinetic data, led to the equilibrium constant ($K=0.68$) of reaction (14) at 333 K, in chlorobenzene ($RO_2^{\bullet}=\mathbf{1}$). Assuming a negligible entropy change for the reaction, $\Delta_r H \approx \Delta_r G = 1.1$ kJ mol^{-1}.[30,31] This reaction enthalpy can then be equated to the difference $D_{sln}(PhO-H) - D_{sln}(RO_2-H)$, i.e., the PhO–H bond dissociation enthalpy can be derived if $D_{sln}(RO_2-H)$ is known. Mahoney and DaRooge used $D_{sln}(RO_2-H) = 368.2 \pm 7.1$ kJ mol^{-1}, a "universal" value accepted for organic hydroperoxides,[30] implying $D_{sln}(PhO-H) = 369.3 \pm 8$ kJ mol^{-1}. Although this result looks sensible in comparison with the gas phase data, the value for $D_{sln}(RO_2-H)$ deserves further discussion.

$$RO_2^{\bullet}(sln) + PhOH(sln) \rightleftharpoons RO_2H(sln) + PhO^{\bullet}(sln). \quad (14)$$



1

The difference between the enthalpies of formation of an organic peroxy radical and its hydroperoxide in solution (tetralin–chlorobenzene) has been investigated by Mahoney and DaRooge.[32] The rate constants of the forward and reverse reactions of equilibrium (15) as a function of temperature (range 303–333 K) have been determined for $R=$ tetralylperoxy radical (**3**), i.e., the peroxy radical derived from 1,2,3,4-tetrahydronaphthalene (tetralin). The reaction enthalpy, -29.3 ± 7.1 kJ mol^{-1}, yields the difference between the enthalpies of formation of $RO_2^{\bullet}$ and RO_2H if the difference between the enthalpies of formation of 2,4,6-tri-*tert*-butylphenol (**2**) and its phenoxy radical are known. Before addressing this final step, it must be stressed that, based on kinetic evidence, Mahoney and DaRooge concluded that the enthalpy of reaction (15) will be insensitive to the structure of the peroxy radical.[32] In other words, the enthalpy should be nearly the same for $RO_2^{\bullet}=\mathbf{1}$.



2 3

(15)

The difference between the enthalpies of formation of 2,4,6-tri-*tert*-butylphenol and its phenoxy radical was determined by reaction–solution calorimetry.[33] First, the enthalpy of reaction (16) (AH=**2**) in a tetralin–chlorobenzene mixture was measured as -143.5 ± 0.5 kJ mol^{-1}. Then, using the enthalpies of solution of hydrazobenzene (22.5 ± 0.3 kJ mol^{-1}) and *trans*-azobenzene (21.9 ± 0.04 kJ mol^{-1}) and the recommended enthalpies of formation of these crystalline compounds (Appendix), one obtains $\Delta_f H^{\circ}_m(AH,sln) - \Delta_f H^{\circ}_m(A^{\bullet},sln) = -115.1 \pm 1.2$ kJ mol^{-1}.[34] It is now possible to derive the difference between the enthalpies of formation of an organic peroxy radical and its hydroperoxide, using this result and the enthalpy of reaction (15): $\Delta_f H^{\circ}_m(RO_2^{\bullet},sln) - \Delta_f H^{\circ}_m(RO_2H,sln) = 144.4 \pm 7.2$ kJ mol^{-1}. If it is assumed, as Mahoney and DaRooge implicitly did, that the enthalpy of solvation of the hydrogen atom is negligible, the previous result corresponds to $D_{sln}(RO_2-H) = 362.4 \pm 7.2$ kJ mol^{-1}, which is ~ 8 kJ mol^{-1} lower than the value accepted by those authors (see above).

$$2A^{\bullet}(sln) + N_2H_2Ph_2(sln) \rightarrow 2AH(sln) + \textit{trans}\text{-}N_2Ph_2(sln). \quad (16)$$

Assuming, as remarked before, that $\Delta_f H^{\circ}_m(RO_2^{\bullet},sln) - \Delta_f H^{\circ}_m(RO_2H,sln) = 144.4 \pm 7.2$ kJ mol^{-1} is similar for $RO_2^{\bullet}=\mathbf{1}$ and **3**, then this value can finally be associated with the enthalpy of reaction (14) to give $\Delta_f H^{\circ}_m(PhO^{\bullet},sln) - \Delta_f H^{\circ}_m(PhOH,sln) = 145.5 \pm 7.2$ kJ mol^{-1} and $D_{sln}(PhO-H) = 368.5 \pm 7.3$ kJ mol^{-1}.

It is now appropriate to discuss the solvation energetics of the phenoxy radical *versus* phenol. As stated after Scheme 1, the premise that the solvation enthalpies of those species are identical does not apply for solvents which have the ability of forming hydrogen bonds to phenol. Wayner *et al.*[28] have made the reasonable assumption that the difference $\Delta_{sln}H(PhOH,g) - \Delta_{sln}H(PhO^{\bullet},g)$ is simply given by the enthalpy of the hydrogen bond between phenol and the solvent,

PhOH–S. Although, this issue has been covered by abundant experimental data,[35] we will use the ECW model,[36,37] whose reliability is probably better than 1 kJ mol^{-1} for the type of interaction under study. To the best of our knowledge, the parameters for chlorobenzene are not available, but the interaction between this solvent and phenol must be slightly stronger than with benzene.[38] A value of -9 ± 2 kJ mol^{-1} is accepted for $\Delta_{sln}H(PhOH,g)-\Delta_{sln}H(PhO^{\bullet},g)$ in chlorobenzene, which, together with $\Delta_fH^o_m(PhO^{\bullet},sln)-\Delta_fH^o_m(PhOH,sln)=145.5\pm7.2$ kJ mol^{-1} derived above, leads to $D(PhO-H)=354.5\pm7.5$ kJ mol^{-1}.

The "electrochemical method" to derive bond dissociation enthalpies has been described in detail[28,29,39] and only a brief discussion is given here, for the sake of clarity. The bond dissociation Gibbs energy, $DG_{sln}(R-H)$, of a molecule RH, in a given solvent S, is related [Scheme 2 and Eq. (17)] to the pK_a of RH, to the standard oxidation potential of the anion, $-E^o_{NHE(aq)}(R^{\bullet}/R^-)_S$, and to the standard reduction potential of the hydride, $E^o_{NHE(aq)}(H^+/H^{\bullet})_S$, both referred to the normal hydrogen electrode in water, NHE(aq). F is the Faraday constant.

$RH(sln)\rightleftharpoons R^-(sln)+H^+(sln)$	$2.303RTpK_{RH}$
$R^-(sln)\rightleftharpoons R^{\bullet}(sln)+e^-$	$FE^o_{NHE(aq)}(R^{\bullet}/R^-)_S$
$H^+(sln)+e^-\rightleftharpoons H^{\bullet}(sln)$	$-FE^o_{NHE(aq)}(H^+/H^{\bullet})_S$
$RH(sln)\rightleftharpoons R^{\bullet}(sln)+H^{\bullet}(sln)$	$DG_{sln}(R-H)$

Scheme 2

$$DG_{sln}(R-H)=2.303RTpK_{RH}+FE^o_{NHE(aq)}(R^{\bullet}/R^-)_S-FE^o_{NHE(aq)}(H^+/H^{\bullet})_S. \quad (17)$$

The application of Eq. (17) requires an estimate of the reduction potential of H^+ in the same solvent where the experiments were carried out. It is simple to conclude [Eq. (18)], through a thermochemical cycle,[29,40] that $E^o_{NHE(aq)}(H^+/H^{\bullet})_S$ depends on thermodynamic parameters of the gaseous hydrogen atom (the Gibbs energy of formation and the Gibbs energy of solvation in the solvent S) and of the proton (the Gibbs energy of transfer from S to water).

$$-FE^o_{NHE(aq)}(H^+/H^{\bullet})_S=\Delta_fG^o(H^{\bullet},g)+\Delta_{sln}G(H^{\bullet},g)+\Delta_{transf}G(H^+,S\rightarrow aq). \quad (18)$$

Once $DG_{sln}(R-H)$ is known, the R–H bond dissociation enthalpy in the solvent S can be derived through Eq. (19). The calculation requires, however, an estimate for the solvation entropies of H$^{\bullet}$, R$^{\bullet}$ and RH. It is often assumed that the solvation entropies of the latter two species are identical.

$$D_{sln}(R-H)=DG_{sln}(R-H)+T[S^o(H^{\bullet},g)+S^o(R^{\bullet},g)-S^o(RH,g)]+T[\Delta_{sln}S(H^{\bullet},g)+\Delta_{sln}S(R^{\bullet},g)-\Delta_{sln}S(RH,g)]. \quad (19)$$

Finally, the R–H bond dissociation enthalpy in the gas phase can be obtained from Eq. (20), which includes the solvation enthalpies of RH and R$^{\bullet}$

$$D(R-H)=2.303RTpK_{RH}+FE^o_{NHE(aq)}(R^{\bullet}/R^-)_S+\Delta_{transf}G(H^+,S\rightarrow aq)+\Delta_fH^o(H^{\bullet},g)+0.5TS^o(H_2,g)+T[S^o(R^{\bullet},g)-S^o(RH,g)]+T[\Delta_{sln}S(R^{\bullet},g)-\Delta_{sln}S(RH,g)]+\Delta_{sln}H(RH,g)-\Delta_{sln}H(R^{\bullet},g). \quad (20)$$

Equation (20) can be simplified by canceling the solvation entropies and enthalpies of R$^{\bullet}$ and RH. As referred to above, while for many species and solvents these approximations are thought to be sensible, in the case of phenol they may lead to a significant error.[28] Nevertheless, this was the approach used by Bordwell and co-workers.[40] In fact, Bordwell's group combined most of the terms of Eq. (20) in a single constant, C, which was empirically adjusted to give better agreement with gas phase data.[41,42] Equation (21) illustrates this procedure. $C=306.7$ kJ mol^{-1} is valid for S=dimethylsulphoxide and when the oxidation potential of R$^-$ is referred to the ferrocene/ferrocenium (Fc/Fc^+) couple instead of the NHE in water.

$$D(R-H)=2.303RTpK_{RH}+FE^o_{Fc/Fc^+}(R^{\bullet}/R^-)_{DMSO}+306.7. \quad (21)$$

In the case of phenoxy radical,[40,43–45] Eq. (21) and the most recent data [$pK_{PhOH}=18.0$, $E^o_{Fc/Fc^+}(PhO^{\bullet}/PhO^-)_{DMSO}=-0.325$ V][44] lead to $D(PhO-H)=378.1$ kJ mol^{-1} at 298 K.

As remarked above, the constant in Eq. (21) was set to yield the best agreement between gas phase and solution data for a variety of bonds. The issue has been reviewed in a recent paper by Bordwell and Liu,[45] the conclusion being that, with few exceptions, the results derived from Eq. (21) "are within $\sim\pm8$ kJ mol^{-1} of the literature values." This agreement even includes some O–H bonds in molecules such as alcohols and substituted phenols, which are known to have specific interactions with proton–acceptor solvents. It must be kept in mind, however, that the "literature values" are often subject to uncertainties (as abundantly illustrated in the present paper), which are in the range of the solvation effects under discussion. Therefore, the controversy of applying solvation corrections to Eq. (21)[28,45] cannot be settled before more accurate gas-phase data are available. Nevertheless, in the case of phenol, as recognized by Bordwell and Liu, that correction must be applied. Using the ECW parameters for phenol and dimethylsulphoxide,[37] $\Delta_{sln}H(PhOH,g)-\Delta_{sln}H(PhO^{\bullet},g)=-29.4$ kJ mol^{-1} is obtained, implying that the final gas-phase value, derived from Bordwell's

method, amounts to $D(\text{PhO–H}) = 348.7$ kJ mol^{-1}.[46]

One of the major error sources of the electrochemical method is the irreversibility of the oxidation potential of R^-.[39,47] As stated by Lind *et al.*,[48(a)] the phenoxy radical has a short lifetime and it is more easily oxidized than the phenolate. The measurement is also complicated by secondary reactions, such as the dimerization of the radical,[48(a)] which is the most common fate of the free radicals formed upon oxidation or reduction of ions in solution.[39] The dimerization leads to a kinetic shift of the measured peak potential of the anion, used to evaluate its standard oxidation potential, $-E^\circ_{\text{NHE(aq)}}(R^\bullet/R^-)_S$ in Eq. (17).[39] When the dimerization rate constant is 10^9 M^{-1} s^{-1}, that kinetic shift leads to an error in the bond dissociation enthalpy of about 17 kJ mol^{-1}. Bordwell and co-workers take this phenomenon into account in the empirical constant C [see Eq. (21)]. However, when the oxidation of the phenoxide is reversible, as for hindered phenols, the kinetic shift does not occur and the bond dissociation enthalpies derived with Eq. (21) may be overestimated.[48(b)] In order to avoid these problems, Lind *et al.* have used pulse radiolysis to establish equilibria in aqueous solution, illustrated by Eq. (22). Here, D$^\bullet$ is an electron donor radical and D^- its parent anion.

$$\text{PhO}^\bullet(\text{aq}) + \text{D}^-(\text{aq}) \rightleftharpoons \text{PhO}^-(\text{aq}) + \text{D}^\bullet(\text{aq}). \qquad (22)$$

The determination of the equilibrium constant of reaction 22 at 298 K affords $E^\circ_{\text{NHE(aq)}}(\text{PhO}^\bullet/\text{PhO}^-)_{\text{aq}}$ if $E^\circ_{\text{NHE(aq)}}(\text{D}^\bullet/\text{D}^-)_{\text{aq}}$ is known. This methodology led to 0.79 ± 0.01 V for the oxidation potential of PhO^-, which, together with $pK_a = 10.0$,[48(a)] Eq. (20), and auxiliary data in the Appendix, yields $D(\text{PhO–H}) = 356.4$ kJ mol^{-1}. It must be stressed that all the solvation correction terms are included in this value.[49]

Hoping to avoid the problem of measuring the reversible oxidation potential of phenoxide anion by cyclic voltammetry, Arnett *et al.*[50(a)] have used a different technique (second-harmonic ac voltammetry) to obtain $E^\circ_{\text{NHE(aq)}}(\text{PhO}^\bullet/\text{PhO}^-) = -0.270 \pm 0.010$ V in a 5% solution of 3-methylsulfolane in sulfolane (tetramethylene sulfone).[50(b)] Assuming that the pK_a of phenol in this solvent is close to the value measured in dimethylsulphoxide (18.0), $D(\text{PhO–H}) = 383.4$ kJ mol^{-1}, is derived from Eq. (21). When the correction $\Delta_{\text{sln}}H(\text{PhOH,g}) - \Delta_{\text{sln}}H(\text{PhO}^\bullet\text{,g}) = -29.4$ kJ mol^{-1} is included (see above), $D(\text{PhO–H}) = 354.0$ kJ mol^{-1} is obtained.[46]

Photoacoustic calorimetry (PAC) has been widely used to probe the energetics of many transient species,[51] including the phenoxy radical.[28,52] The experimental approach is described in Scheme 3: the photochemically produced *tert*-butoxy radical abstracts the hydroxylic hydrogen from phenol, yielding PhO$^\bullet$.

$$t\text{-BuOOBu-}t(\text{sln}) \xrightarrow{h\nu} 2t\text{-BuO}^\bullet(\text{sln})$$

$$2\text{PhOH(sln)} + 2t\text{-BuO}^\bullet(\text{sln}) \rightarrow 2\text{PhO}^\bullet(\text{sln}) + 2t\text{-BuOH(sln)}$$

$$t\text{-BuOOBu-}t(\text{sln}) + 2\text{PhOH(sln)} \rightarrow 2\text{PhO}^\bullet(\text{sln}) + 2t\text{-BuOH(sln)} \qquad (23)$$

Scheme 3

The PAC determination of the net reaction enthalpy in Scheme 3 involves a simple enthalpy balance. Part of the energy of the absorbed laser photons ($E_0 = 354.9$ kJ mol^{-1} for a nitrogen laser), is used to cleave the O–O bond in *t*-BuOOBu-*t*, thus initiating the chain reaction. The remaining laser energy, increased or decreased by the exo- or endothermicity of the fast hydrogen abstraction reaction, is deposited in solution and produces a shock wave. This heat ($\Delta_{\text{obs}}H$), which can be determined because it is proportional to the wave amplitude, is then related, by Eq. (24), to the enthalpy of the net reaction in Scheme 3. Φ is the quantum yield of the di-*tert*-butylperoxide homolysis

$$\Delta_r H = \frac{354.9 - \Delta_{\text{obs}}H}{\Phi} + \frac{\Delta V}{\chi}. \qquad (24)$$

The last term in Eq. (24) represents a correction due to the so-called nonthermal expansion. If a reaction is accompanied by a non-negligible molar volume change (ΔV), as in the case of Scheme 3, a fraction of the observed wave amplitude will be due to that physical expansion, i.e., the true value of the heat deposition will be less than the one observed. This, in turn, implies a positive correction of $\Delta_r H(23)$. The volume change of the net reaction has been estimated by Wayner *et al.*[28] as ~13 mL/mol, under the assumption that the main contribution comes from the homolysis of di-*tert*-butylperoxide. The parameter χ, which depends on the isobaric expansion coefficient, the molar heat capacity, and the density of the solvent,[53] has also been calculated for several solvents by the same authors.[28] Using these data, it is noted that the resulting $\Delta V/\chi$ values fall in a narrow range. For instance, considering acetonitrile, ethylacetate, isooctane, benzene, and carbon tetrachloride, the average $\Delta V/\chi$ is 16.0 kJ mol^{-1}, with a standard deviation of 0.3 kJ mol^{-1}.

As evidenced by Eq. (25), the calculation of the solution phase PhO–H bond dissociation enthalpy from $\Delta_r H(23)$ requires three solution terms. With exception of the solvation enthalpy of the hydrogen atom (see above), those quantities can be easily measured by reaction–solution calorimetry. A different approach was, however, followed by Wayner *et al.*[28]

$$\begin{aligned} D_{\text{sln}}(\text{PhO–H}) = {} & \Delta_r H(23)/2 + \Delta_f H^\circ_{\text{m}}(\text{H}^\bullet\text{,g}) + \Delta_{\text{sln}}H(\text{H}^\bullet\text{,g}) \\ & + \Delta_f H^\circ_{\text{m}}(t\text{-BuOOBu-}t\text{,l})/2 \\ & - \Delta_f H^\circ_{\text{m}}(t\text{-BuOH,l}) \\ & + \Delta_{\text{sln}}H^\circ(t\text{-BuOOBu-}t\text{,l})/2 \\ & - \Delta_{\text{sln}}H^\circ(t\text{-BuOH,l}). \end{aligned} \qquad (25)$$

In order to avoid the direct measurements of the last two solution enthalpies in Eq. (25), the authors used the "reference" reaction (26), whose steps are identical to those in Scheme 3, the only difference being that the phenol is replaced by 1,4-cyclohexadiene and the cyclohexadienyl radical is produced.

$$t\text{-BuOOBu-}t(\text{sln}) + 2cy\text{-}C_6H_8(\text{sln}) \rightarrow 2cy\text{-}C_6H_7^{\bullet}(\text{sln}) + 2t\text{-BuOH(sln)}. \quad (26)$$

The PAC study and subsequent analysis of reaction (26) yields an equation similar to (25) and allows us to express D_{sln}(PhO–H) in terms of the gas-phase C–H bond dissociation enthalpy [Eq. (27)], under the assumption that 1,4-cyclohexadiene and the cyclohexadienyl radical have the same solvation enthalpies. The main advantage of this methodology [versus Eq. (25)] is that it does not require us to estimate the correction term $\Delta V/\chi$, since it is reasonable to assume that reactions (23) and (26) have similar volume changes. Also, Eq. (27) does not depend on the thermochemical data for di-*tert*-butylperoxide and *tert*-butanol. The drawback is, of course, that it relies on the anchor D(C–H)

$$D_{sln}(\text{PhO–H}) = D(\text{C–H}) + [\Delta_r H(23) - \Delta_r H(26)]/2 + \Delta H_{sln}(\text{H}^{\bullet},\text{g}). \quad (27)$$

Tsang[54] has made a critical analysis of the experimental values for the enthalpy of formation of cyclohexadienyl radical and recommended 209±5 kJ mol^{-1}. Using the most recent auxiliary data for the enthalpy of formation of 1,4-cyclohexadiene (100.4±5.9 kJ mol^{-1}),[2] one obtains D(C–H) = 326.6±5.9 kJ mol^{-1}.[55] This value and the PAC experimental data by Wayner *et al.*[28] lead to the PhO–H bond dissociation enthalpies displayed in Table 3. The gas phase data were calculated with Eq. (28), the solution terms being estimated with the ECW model, as described above

$$D(\text{PhO–H}) = D(\text{C–H}) + [\Delta_r H(23) - \Delta_r H(26)]/2 + \Delta_{sln}H(\text{PhOH,g}) - \Delta_{sln}H(\text{PhO}^{\bullet},\text{g}). \quad (28)$$

The most recent value for D_{sln}(PhO–H) reported in the literature, here recalculated as 363.6±3.6 kJ mol^{-1}, relies on electron spin resonance (ESR) equilibrium studies in benzene by Lucarini *et al.*[56] and it is anchored on 334.1±1.2 kJ mol^{-1} for the O–H bond dissociation enthalpy of 2,4,6-tri-*tert*-butylphenol in benzene, which is based on the results by Mahoney, Ferris, and DaRooge (see Sec. 5).[33] The studies by Lucarini *et al.* are further discussed in Sec. 5. The corresponding gas phase D(PhO–H) value, 349.9 kJ mol^{-1}, was derived [Eq. (13)] from the solution result, from $\Delta_{sln}H(\text{H}^{\bullet},\text{g}) = 5 \pm 1$ kJ mol^{-1} (see above), and from $\Delta_{sln}H(\text{PhOH,g}) - \Delta_{sln}H(\text{PhO}^{\bullet},\text{g}) = -8.7$ kJ mol^{-1}.[36,37]

4. The PhO–H Bond Dissociation Enthalpy: Recommended Data

The results of the gas phase and solution phase studies on the energetics of PhO–H bond are summarized in Tables 2 and 3. Although the data for the bond dissociation enthalpy are apparently in striking disagreement (they span 30 kJ mol^{-1}!), the discussion above provides some ground to select a value with a fairly small error bar.

As the results in Table 2 do not rely on any complicating solvation data, it seems reasonable to consider that they are more accurate than those displayed in Table 3. It is observed that almost all the PhO–H bond dissociation enthalpy values in Table 2 fall in the range of ~365–375 kJ mol^{-1}. The exceptions are the three oldest results, the evaluation by Back (361.4 kJ mol^{-1}),[10] and one of the values by Walker and Tsang (363.6 kJ mol^{-1}).[16] As discussed above, the bond dissociation enthalpy derived by Back is an average involving the first entry in Table 2 (348.5 kJ mol^{-1}), which looks too low. Walker and Tsang, on the other hand, rather than recommending an average of D(PhO–H) calculated from reaction (3) (363.6 kJ mol^{-1}), endorse the value based on reaction (5) (369.3 kJ mol^{-1}). Therefore, our choice for the gas-phase PhO–H bond dissociation enthalpy is based simply on the average of all the starred values in Table 2: D(PhO–H) = 371.3±2.3 kJ mol^{-1} (the uncertainty is twice the standard deviation of the mean). This corresponds to $\Delta_f H^{\circ}_m(\text{PhO}^{\bullet},\text{g}) = 56.9 \pm 2.4$ kJ mol^{-1}. Interestingly, this value is very close to the one endorsed 30 years ago by Fine and Westmore, and by Laye *et al.*[6,7]

Our selection for D(PhO–H) is only slightly higher than Tsang's recent recommendation, 368.4±6.1 kJ mol^{-1}.[4] It is also in agreement with the average value of the PAC results, 373.3±5.4 kJ mol^{-1}, which are considered the most reliable values in Table 3.

TABLE 2. Recalculated values of the standard enthalpy of formation of PhO$^{\bullet}$ and the PhO–H bond dissociation enthalpy (T = 298 K), determined by gas phase methods. Data in kJ mol^{-1}

Method[a]	$\Delta_f H^{\circ}_m$(PhO$^{\bullet}$,g)	D(PhO–H)[b]	Year and Ref.
SR/TS	34.1±8.5	348.5±8.5	1975 (8)
VLPP	47.4±8.0	361.8±8.1	1977 (11)
BR-ICR	46.0±8.4	360.4±8.4	1980 (18)
IMRE/PES	51.9±8	366.3±8*	1981, 1992 (23–25)
SHTU/EVAL	57.7±8[c]	372.1±8*	1986, 1996 (14, 4)
FR	60.6±2.8	375.0±2.9*	1989 (9)
VLPP	59.9	374.3*	1989 (15)
FR/SR/EVAL	47.0±8.5	361.4±8.5	1989 (8–10)
SPST	49.2	363.6	1990 (16)
SPST	54.9	369.3*	1990 (16)
FR	58.0	372.4*	1993 (17)
MS-KM	55.2±8	369.6±8*	1994 (19)
Recommended	**56.9±2.4**	**371.3±2.3**	This paper

[a](BR-ICR) bracketing reactions, ion-cyclotron resonance mass spectrometry; (EVAL) literature evaluation; (FR) flow reactor; (IMRE) ion-molecule reaction equilibrium; (MS-KM) mass spectrometry, kinetic method; (PES) photoelectron spectroscopy; (SHTU) shock tubes; (SPST) single-pulse shock tubes; (SR) static reactor; (TS) toluene scavenging; (VLPP) very low pressure pyrolysis.

[b]The starred values are considered the most reliable.

[c]Tsang (Ref. 4) recommended $\Delta_f H^{\circ}$(PhO$^{\bullet}$,g) = 54±6 kJ mol^{-1}, which implies D(PhO–H) = 368.4±6.1 kJ mol^{-1}.

5. The O–H Bond Dissociation Enthalpies in Substituted Phenols: Solution Studies

There is a wealth of literature studies addressing the energetics of the O–H bond in substituted phenols. Nevertheless, as discussed above for the case of phenol itself, a comparison

TABLE 3. Recalculated values of the PhO–H bond dissociation enthalpy from solution studies. Data in kJ mol^{-1}

Method[a]	Solvent	D_{sln}(PhO–H)[b]	$-\Delta H$(ECW)[c]	D(PhO–H)[d]	Year and Ref.
K/Eq/RSC	chlorobenzene	368.5±7.3	(9±2)	354.5±7.5	1975 (30)
EChem	dimethylsulphoxide	378.1	29.4	348.7[e]	1988, 1995 (40, 44)
Eq/EChem	water			356.4	1990 [48(a)]
EChem	sulfolane	383.4	(29.4)	354.0[e]	1990 [50(a)]
PAC	benzene	378.7	8.7	365.0	1988, 1995 (52, 28)
PAC	isooctane	373.9	(0)	368.9	1995 (28)
PAC	carbon tetrachloride	381.6	(0)	376.6	1995 (28)
PAC	acetonitrile	402.3	18.7	378.6	1995 (28)
PAC	ethyl acetate	402.1	19.8	377.3	1995 (28)
Eq	benzene	363.6±3.6	8.7	349.9	1996 (56)

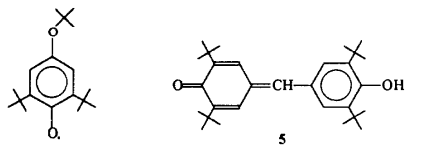
[a](EChem) electrochemical methods; (Eq) equilibrium methods; (K) kinetic methods; (PAC) photoacoustic calorimetry; (RSC) reaction-solution calorimetry.
[b]Solution phase bond dissociation enthalpy.
[c]$\Delta H(\mathrm{ECW}) = \Delta_{sln}H(\mathrm{PhOH,g}) - \Delta_{sln}H(\mathrm{PhO^{\bullet}},\mathrm{g})$. Calculated from the ECW model (Refs. 36 and 37). Estimated values in parentheses.
[d]Gas phase bond dissociation enthalpy.
[e]See Ref. 46.

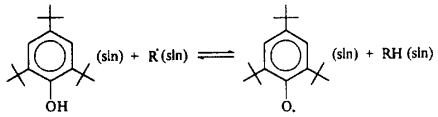
of these data is often hindered by the use of different anchors or assumptions. To avoid this difficulty, and also because the main interest is investigating the substituent effect on D(O–H), it is preferable to tabulate the bond dissociation enthalpies relative to D(PhO–H) and/or D_{sln}(PhO–H). These relative quantities, represented by ΔD(O–H) and ΔD_{sln}(O–H), respectively, are analyzed in the following paragraphs and collected in Table 4. We shall start by reviewing the data obtained from solution methods.

One of the first studies probing the energetics of O–H bonds in substituted phenols was based on equilibria similar to reaction (14).[30] The method and assumptions were identical to those noted above and the trend was claimed to be reliable within ±2.1 kJ mol^{-1}.

Reaction–solution calorimetry experiments involving reaction (16) for 2,4,6-tri-*tert*-butylphenol (AH=**2**) allowed us to derive D_{sln}(O–H) in several solvents.[33] These data, which have been recalculated as described in Sec. 3 for the difference $\Delta_f H^{\circ}_m$(AH,sln) − $\Delta_f H^{\circ}_m$(A$^{\bullet}$,sln)(AH=**2**) in a tetralin–chlorobenzene mixture, are as follows (kJ mol^{-1}): 330.1±1.3 (carbon tetrachloride), 334.1±1.2 (benzene), 330.0±1.2 (chlorobenzene), and 333.1±1.2 (tetralin–chlorobenzene). The only relative value shown in Table 4 from this set of data is anchored on D_{sln}(PhO–H)=368.5 kJ mol^{-1} (from Table 3).

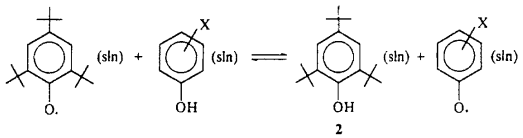
Mahoney, Ferris, and DaRooge, in the same paper where the O–H bond dissociation enthalpy in 2,4,6-tri-*tert*-butylphenol was derived,[33] used a literature value for the enthalpy of reaction (29), 14.3±0.7 kJ mol^{-1},[57] to derive D_{sln}(O–H) for R$^{\bullet}$=**4** in benzene. The recalculated value, D_{sln}(O–H)=319.8±1.4 kJ mol^{-1}, is shown in Table 4 relative to D_{sln}(PhO–H)=368.5 kJ mol^{-1}. It must be noted, however, that the solvent for this anchor is chlorobenzene instead of benzene. As observed in the previous paragraph, the O–H bond dissociation enthalpy of 2,4,6-tri-*tert*-butylphenol in benzene is 4.1 kJ mol^{-1} higher than in chlorobenzene. If the difference applies to phenol, then the value in Table 4 should be 4 kJ mol^{-1} more negative. The same approach has been used to calculate the O–H bond dissociation enthalpies in the remaining two RH compounds addressed in Mahoney, Ferris, and DaRooge's paper (**5** and **6**), also shown in Table 4.



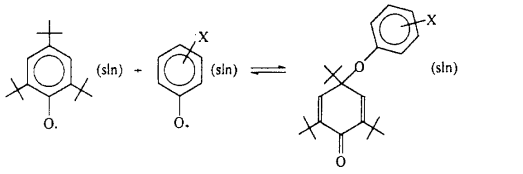


(29)

Mahoney and DaRooge have also probed the thermochemistry of the combined reactions (30) and (31) in chlorobenzene, by reaction–solution calorimetry, for several X.[58] Each O–H bond dissociation enthalpy in the substituted phenol can be anchored on D_{sln}(O–H)=330.0±1.2 kJ mol^{-1} in 2,4,6-tri-*tert*-butylphenol (see above), as shown by Eq. (32). Here, $\Delta_r H(30+31)$ is the enthalpy of the net reaction and ΔE_a represent the difference between the forward and reverse activation energies of reaction (31)



(30)



(31)

TABLE 4. Values of the O–H bond dissociation enthalpies ($T=298$ K) in substituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}

Substituent	Method[a]	Solvent	ΔD_{sln}(O–H)[b]	ΔD(O–H)[c]	Ref.
Monosubstituted phenols					
2-Me	EChem	dimethylsulphoxide	−7.0		43
	VLPP			−10.9	78
	AM1			−6.7	78
(away)[d]	AM1/DFT[e]			−6.7	81
(toward)[d]	AM1/DFT[e]			−11.1	81
	Selected			**−9±4**	
3-Me	EChem	dimethylsulphoxide	−1.9		43
	MS-KM			−5.9	19
	VLPP			−2.1	78
	AM1			0.8	78
(away)[d]	AM1/DFT[e]			−5.2	81
(toward)[d]	AM1/DFT[e]			−1.4	81
	Selected			**−3±4**	
4-Me	EChem	dimethylsulphoxide	−4.8		43
	K/Eq	chlorobenzene	−7.2		30
	EChem	sulfolane	−18.6		50(a)
	EChem	water		−8.9	48(a)
	Eq	benzene	−8.8		56
	VLPP			−7.9	78
	AM1			−5.9	78
	AM1/DFT[e]			−8.0	81
	DFT[f]			−7.5	82
	DFT[g]			−12.2	79
	DFT[h]			−7.9	79
	Selected			**−8±4**	
2-$CHCH_2$	VLPP			−10.0	78
	AM1			−11.7	78
	Selected			**−10±8**	
4-*t*-Bu	EChem	dimethylsulphoxide	−4.6		43
	K/Eq	chlorobenzene	−7.4		30
	RSC/K	chlorobenzene	−2.7		58
	EChem	sulfolane	−7.1		50(a)
	PAC	benzene	−8.2		52
	Eq	benzene	−12.6		56
	Selected			**−7±4**	
4-Ph	EChem	dimethylsulphoxide	−9.5		43
	K/Eq	chlorobenzene	−13.6		30
	Selected			**−12±4**	
4-O^-	EChem	dimethylsulphoxide	−70.3		43
	EChem	water		−66.0	48(a)
	DFT[g]			−146.1	79
	DFT[h]			−138.0	79
	Selected			**−68±8**	
4-O$^\cdot$	EChem	water		−101.8	62
	Selected			**−102±13**	
2-OH	VLPP			−30.1	15
	AM1			−25.1	78
	Selected			**−30±8**	
3-OH	VLPP			1.3	15
	AM1			2.5	78
	Selected			**1±8**	
4-OH	EChem	dimethylsulphoxide	−34.8		43
	EChem	water		−33.5	48(a)
	EChem	water		−28.7	62
	VLPP			−10.5	15
	AM1			−16.7	78
	DFT[f]			−22.6	82
	DFT[g]			−26.7	79
	DFT[h]			−26.3	79
	Selected			**−27±10**	
2-OMe	EChem	dimethylsulphoxide	−16.2		43
	VLPP			−17.6	15
	AM1			−22.2	78

TABLE 4. Values of the O–H bond dissociation enthalpies (T = 298 K) in substituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}—Continued

Substituent	Method[a]	Solvent	ΔD_{sln}(O–H)[b]	ΔD(O–H)[c]	Ref.
(away)[d]	AM1/DFT[e]			−18.2	81
(toward)[d]	AM1/DFT[e]			5.6	81
	Selected			**−17±4**	
3-OMe	EChem	dimethylsulphoxide	1.4		43
	VLPP			−4.2	15
	AM1			0.4	78
	Selected			**0±4**	
4-OMe	EChem	dimethylsulphoxide	−22.0		43
	K/Eq	chlorobenzene	−17.5		30
	RSC/K	chlorobenzene	−25.2		58
	EChem	sulfolane	−22.0		50(a)
	EChem	water		−23.5	48(a)
	PAC	benzene	−25.3		52
	PAC	benzene	−24.9	−16.2	67
	Eq	benzene	−23.0		56
	K	heptanol	−24.3		75
	VLPP			−16.3	15
	AM1			−17.2	78
	AM1/DFT[e]			−18.6	81
	DFT[f]			−23.0	82
	DFT[g]			−29.6	79
	DFT[h]			−25.1	79
	Selected			**−22±4**	
2-CH_2OH	VLPP			−10.0	78
	AM1			−4.2	78
	Selected			**−10±8**	
2-COMe	VLPP			−5.9	78
	AM1			0	78
	Selected			**−6±8**	
3-COMe	EChem	dimethylsulphoxide	8.4		43
	VLPP			1.3	78
	AM1			2.5	78
	Selected			**5±4**	
4-COMe	EChem	dimethylsulphoxide	12.4		43
	EChem	water		8.9	48(a)
	VLPP			2.5	78
	AM1			7.9	78
	DFT[g]			7.0	79
	DFT[h]			7.9	79
	Selected			**9±5**	
3-COEt	RSC/K	chlorobenzene	9.2		58
	Selected			**9±10**	
4-COPh	EChem	dimethylsulphoxide	11.1		43
	Selected			**11±10**	
4-CO_2^-	EChem	water		7.2	48(a)
	Selected			**7±10**	
4-OCOMe	EChem	sulfolane	−11.2		50(a)
	Selected			**−11±10**	
3-COOEt	K/Eq	chlorobenzene	6.7		30
	Selected			**7±8**	
2-NH_2	VLPP			−31.0	78
	AM1			−43.1	78
(away)[d]	AM1/DFT[e]			−52.9	81
(toward)[d]	AM1/DFT[e]			−60.7	81
	Selected			**−31±10**	
3-NH_2	EChem	dimethylsulphoxide	−7.6		43
	VLPP			−1.7	78
	AM1			3.3	78
	Selected			**−5±4**	
4-NH_2	EChem	dimethylsulphoxide	−52.4		43
	EChem	water		−53.0	48(a)
	VLPP			−12.1	78
	AM1			−30.1	78
	AM1/DFT[e]			−36.9	81
	DFT[f]			−36.0	82

TABLE 4. Values of the O–H bond dissociation enthalpies (T=298 K) in substituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}—Continued

Substituent	Method[a]	Solvent	ΔD_{sln}(O–H)[b]	ΔD(O–H)[c]	Ref.
	DFT[g]			−50.7	79
	DFT[h]			−38.0	79
	Selected			**−40±13**	
3-NMe_2	EChem	dimethylsulphoxide	−8.3		43
	Selected			**−8±10**	
4-NMe_2	EChem	dimethylsulphoxide	−40.1		43
	EChem	water		58.9	48(a)
	DFT[f]			−39.7	82
	DFT[g]			−58.7	79
	DFT[h]			−42.9	79
	Selected			**−50±10**	
2-CN	VLPP			−0.8	78
	AM1			4.2	78
	Selected			**0±8**	
3-CN	EChem	dimethylsulphoxide	17.3		43
	VLPP			4.6	78
	AM1			6.7	78
	Selected			**13±8**	
4-CN	EChem	dimethylsulphoxide	18.4		43
	EChem	sulfolane	6.4		50(a)
	EChem	water		19.9	48(a)
	PAC	benzene	20.9		67
	VLPP			1.3	78
	AM1			7.5	78
	DFT[f]			9.6	82
	DFT[g]			8.5	79
	DFT[h]			8.1	79
	Selected			**18±8**	
2-NO_2	VLPP			−5.4	78
	AM1			10.9	78
	Selected			**−5±8**	
3-NO_2	EChem	dimethylsulphoxide	18.7		43
	EChem	dimethylsulphoxide	19.0		60
	VLPP			−2.1	78
	AM1			10.5	78
	Selected			**19±8**	
4-NO_2	EChem	dimethylsulphoxide	20.6		43
	EChem	dimethylsulphoxide	29.3		60
	EChem	sulfolane	9.4		50(a)
	EChem	water		25.1	48(a)
	VLPP			5.0	78
	AM1			18.0	78
	DFT[f]			18.4	82
	DFT[g]			8.9	79
	DFT[h]			17.1	79
	Selected			**25±8**	
4-CH_2CHNH_2COOH	EChem	water		−7.1	48(a)
	Selected			**−7±8**	
2-F	VLPP			−7.9	78
	AM1			−12.6	78
	Selected			**−8±8**	
3-F	IMRE			6.6	24
	VLPP			3.8	78
	AM1			8.4	78
	Selected			**6±8**	
4-F	EChem	sulfolane	−1.7		50(a)
	EChem	water		−3.5	48(a)
	VLPP			−4.6	78
	AM1			−10.0	78
	DFT[g]			−6.9	79
	DFT[h]			−9.8	79
	Selected			**−4±4**	
2-Cl	EChem	dimethylsulphoxide	0.6		43
	VLPP			−9.2	15

TABLE 4. Values of the O–H bond dissociation enthalpies ($T = 298$ K) in substituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}—Continued

Substituent	Method[a]	Solvent	ΔD_{sln}(O–H)[b]	ΔD(O–H)[c]	Ref.
	AM1			−3.8	78
	Selected			**−3±4**	
3-Cl	EChem	dimethylsulphoxide	8.6		43
	VLPP			0.8	78
	AM1			4.2	78
	DFT[f]			5.0	82
	Selected			**5±4**	
4-Cl	EChem	dimethylsulphoxide	1.8		43
	EChem	sulfolane	7.7		50(a)
	EChem	water		−2.4	48(a)
	PAC	benzene	1.7		52
	VLPP			−4.6	78
	AM1			2.1	78
	DFT[f]			−2.9	82
	DFT[g]			−6.5	79
	DFT[h]			−4.2	79
	Selected			**−1±4**	
2-Br	VLPP			−7.1	15
	AM1			−2.5	78
	Selected			**−7±8**	
4-Br	EChem	dimethylsulphoxide	3.7		43
	RSC/K	chlorobenzene	2.7		58
	EChem	water		−0.5	48(a)
	DFT[f]			−6.5	82
	Selected			**2±4**	
4-I	EChem	water		−1.3	48(a)
	Selected			**−1±10**	
3-CF_3	EChem	dimethylsulphoxide	16.6		43
	PAC	benzene	11.3		67
	Selected			**13±4**	
4-CF_3	EChem	dimethylsulphoxide	23.0		43
	PAC	benzene	13.7		52
	DFT[f]			10.9	82
	DFT[g]			17.5	79
	DFT[h]			9.9	79
	Selected			**17±4**	
3-SO_2Me	EChem	dimethylsulphoxide	10.5		43
	Selected			**11±8**	
4-SO_2Me	EChem	dimethylsulphoxide	21.7		43
	DFT[g]			17.4	79
	DFT[h]			14.4	79
	Selected			**22±8**	
Disubstituted phenols					
2,6-Me_2	K/Eq	chlorobenzene	−13.2		30
	EChem	dimethylsulphoxide	−13.3		43
	Eq	benzene	−15.9		56
	AM1/DFT[e]			−17.6	81
	Selected			**−14±4**	
3,5-Me_2	RSC/K	chlorobenzene	4.5		58
	EChem	dimethylsulphoxide	−3.1		43
	AM1/DFT[e]			−2.1	81
	Selected			**−3±4**	
2,4-*t*-Bu_2	PAC	benzene	−21.6	−12.9	67
	Selected			**−22±8**	
2,6-*t*-Bu_2	EChem	dimethylsulphoxide	−32.4		43
	Eq	benzene	−23.0		56
	Selected			**−26±8**	
3,5-*t*-Bu_2	K/Eq	chlorobenzene	−5.6		30
	Eq	benzene	−7.0		56
	Selected			**−6±4**	
2,6-$(OMe)_2$	Eq	benzene	−21.5		56
	AM1/DFT[e]			−16.9	81

TABLE 4. Values of the O–H bond dissociation enthalpies ($T=298$ K) in substituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}—Continued

Substituent	Method[a]	Solvent	ΔD_{sln}(O–H)[b]	ΔD(O–H)[c]	Ref.
	Selected			**−21±8**	
3,5-(OMe)$_2$	Eq	benzene	−6.7		56
	Selected			**−7±8**	
3,5-Cl$_2$	EChem	dimethylsulphoxide	17.1		43
	EChem	sulfolane	11.2		50(a)
	Selected			**14±4**	
Trisubstituted phenols					
2,4,6-Me$_3$	PAC	benzene	−22.8	−14.1	67
	Eq	benzene	−23.3		56
	AM1/DFT[e]			−25.4	81
	Selected			**−23±4**	
2,6-*t*-Bu$_2$-4-Me	EChem	dimethylsulphoxide	−43.0		44
	PAC	benzene	−32.0	−23.3	67
	Eq	benzene	−44.3		69
	Eq	benzene	−38.1		70
	Eq	benzene	−40.7		71
	Eq	benzene	−30.5		56
	K	benzene	−40.0		76
	K	heptanol	−31.8		75
	Selected			**−32±8**	
2,6-*t*-Bu$_2$-4-Et	EChem	dimethylsulphoxide	−43.4		44
	Selected			**−43±10**	
2,4,6-*t*-Bu$_3$	EChem	dimethylsulphoxide	−34.0		43, 59
	RSC	chlorobenzene	−38.5		33
	K	heptanol	−38.5		75
	Selected			**−37±4**	
2,4,6-Ph$_3$	EChem	dimethylsulphoxide	−23.1		59, 44
	Selected			**−23±10**	
2,6-*t*-Bu$_2$-4-CHO	Eq	benzene	−28.4		70
	Selected			**−28±8**	
2,6-Me$_2$-4-OMe	PAC	benzene	−41.9	−33.2	67
	Selected			**−42±8**	
2,6-*t*-Bu$_2$-4-OMe	EChem	dimethylsulphoxide	−45.3		59, 44
	Eq	benzene	−51.9		70
	Eq	toluene	−53.7		71
	Eq	benzene+toluene	−56.7		72
	Eq	benzene	−41.8		56
	Selected			**−45±4**	
2,6-*t*-Bu$_2$-4-O-*t*-Bu	RSC/Eq	benzene	−48.7		33
	Selected			**−49±8**	
2,6-*t*-Bu$_2$-4-COMe	K	benzene	−26.2		76
	Selected			**−26±8**	
2,6-*t*-Bu$_2$-4-OCOMe	EChem	dimethylsulphoxide	−25.6		59, 44
	Selected			**−26±10**	
2,6-*t*-Bu$_2$-4-CH$_2$NMe$_2$	Eq	benzene	−37.7		70
	Selected			**−38±8**	
2,4,6-(OMe)$_3$	Eq	benzene	−34.7		56
	Selected			**−35±8**	
2,6-Me$_2$-4-NO$_2$	EChem	dimethylsulphoxide	−0.4		44
	Selected			**0±10**	
2,6-*t*-Bu$_2$-4-NO$_2$	EChem	dimethylsulphoxide	−17.5		44
	EChem	dimethylsulphoxide	−16.1		60
	Eq	benzene	−22.9		70
	Selected			**−19±4**	
2,6-*t*-Bu$_2$-4-CHNOH	Eq	benzene	−43.2		70
	Selected			**−43±8**	
2,4,6-Cl$_3$	RSC/K	chlorobenzene	−1.5		58
	Selected			**−2±8**	
3,4,5-Cl$_3$	EChem	dimethylsulphoxide	13.4		43
	Selected			**13±10**	
2,6-(NO$_2$)$_2$-4-Cl	EChem	dimethylsulphoxide	29.9		60
	EChem	dimethylsulphoxide	15.9		61
	EChem	water	28.5		61

TABLE 4. Values of the O–H bond dissociation enthalpies (T=298 K) in substituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}—Continued

Substituent	Method[a]	Solvent	ΔD_{sln}(O–H)[b]	ΔD(O–H)[c]	Ref.
	Selected			**25±8**	
Other phenols					
2,3,6-Me$_3$-4-OMe	Eq	benzene	−38.1		56
	Selected			**−38±8**	
2,3,5,6-Me$_4$-4-OMe	Eq	benzene	−26.9		56
	AM1/DFT[e]			−29.7	81
	Selected			**−27±8**	
2,3,5,6-F$_4$	IMRE			13.7	24
	Selected			**14±8**	
F$_5$	VLPP			−11.3	78
	AM1			−16.7	78
	Selected			**−11±8**	
1-naphthol (7)	EChem	dimethylsulphoxide	−24.6		43
	VLPP			−24.7	78
	AM1			−22.2	78
	Selected			**−25±4**	
2-naphthol (8)	EChem	dimethylsulphoxide	−7.6		43
	K/Eq	chlorobenzene	−7.4		30
	VLPP			−10.5	78
	AM1			−1.7	78
	Selected			**−8±4**	
5	RSC/Eq	benzene	−45.9		33
	Eq	toluene	−48.7		71
	Selected			**−47±4**	
6	RSC/Eq	benzene	−49.2		33
	Selected			**−49±8**	
17	Eq	benzene	−54.4		70
	Selected			**−54±8**	
19	K	benzene	−49.3		76
	Eq	benzene	−42.0		56
	Selected			**−44±8**	
21	K	benzene	−41.4		76
	Selected			**−41±8**	
***α*-tocopherol (10)**	EChem	dimethylsulphoxide	−40.0		44
	PAC	benzene	−41.7	−33.0	67
	Eq	benzene	−60.4		69
	Eq	benzene	−49.4		70
	Eq	benzene	−48.1		71
	Eq	benzene	−42.1		56
	K	heptanol	−41.8		75
	Selected			**−43±4**	
***δ*-tocopherol (14)**	PAC	benzene	−29.5	−20.8	67
	Selected			**−29±8**	
probucol (18)	Eq	toluene	−39.4		71
	Selected			**−39±8**	
2,4-dinitro-1-naphthol (11)	EChem	dimethylsulphoxide	4.7		60
	Selected			**5±10**	
2-OH-6-Br-naphthalene (9)	EChem	dimethylsulphoxide	−5.5		43
	Selected			**−6±10**	

[a](AM1) Austin Model 1 (semi-empirical MO method); (BR-ICR) bracketing reactions, ion-cyclotron resonance mass spectrometry; (DFT) density functional theory; (EChem) electrochemical methods; (Eq) equilibrium methods; (EVAL) literature evaluation; (FR) flow reactor; (IMRE) ion-molecule reaction equilibrium; (K) kinetic methods; (MS-KM) mass spectrometry, kinetic method; (PAC) photoacoustic calorimetry; (PES) photoelectron spectroscopy; (RSC) reaction-solution calorimetry; (SHTU) shock tubes; (SPST) single-pulse shock tubes; (SR) static reactor; (TS) toluene scavenging; (VLPP) very low pressure pyrolysis.

[b]O–H bond dissociation enthalpy in the substituted phenol minus D_{sln}(PhO–H) in solution.

[c]O–H bond dissociation enthalpy in the substituted phenol minus D(PhO–H) in the gas phase.

[d]"Away" and "toward" mean that the O–H bond is pointed either away from or toward the substituent.

[e]Single point calculations with the B3LYP density functional with a modified 6-31G(,p) basis set. Geometries optimized with the AM1 method.

[f]B3LYP/6-31(d,p) method, used for geometry optimization and energetics.

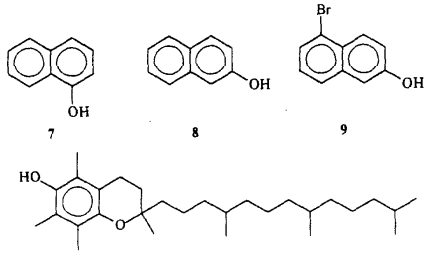
[g]Local density approximation method with a double numerical basis set for geometry optimization (JMW/DN).

[h]BLYP method with a 6-31G(d) basis set.

$$D_{sln}(O-H) = \Delta_r H(30+31) - \Delta E_a + (330.0 \pm 1.2). \quad (32)$$

The problem with the application of Eq. (32) is the quantity ΔE_a. Although Mahoney and DaRooge were able to determine experimental values of the reverse activation energies of reaction (31), they had to assume that the forward activation energies are independent of X. Their estimate for this quantity is ~ 8 kJ mol^{-1}. Although this guess looks reasonable for a radical coupling, it leads to O–H bond dissociation enthalpies which are far too low. For example, in the case of X=4-OMe, $D_{sln}(O-H) = 325.3$ kJ mol^{-1} is obtained, compared to 351.0 kJ mol^{-1} calculated from their later paper (Ref. 30; see Table 4). It is recalled that these results are both relative to $D_{sln}(PhO-H) = 368.5$ kJ mol^{-1}, which is consistent with $D_{sln}(O-H) = 330.0 \pm 1.2$ kJ mol^{-1} in 2,4,6-tri-*tert*-butylphenol. In order to avoid the discrepancy, and once again remembering that the trend of the O–H bond enthalpies is the issue, we have arbitrarily assigned a negative value (-10.0 kJ mol^{-1}) to the forward activation energy of reaction (31). The assumption that this quantity is independent of X is, however, questioned by the final results, (displayed in Table 4), which show poor agreement with those derived later by the same group.[30]

A large number of O–H bond dissociation enthalpies in substituted phenols has been determined by Bordwell's group,[43,44,59] using the electrochemical technique described in Sec. 3. The results (Table 4), which include the compounds **7–10**, are relative to $D_{sln}(PhO-H) = 378.1$ kJ mol^{-1} (Table 3) and were calculated from Eq. (21), using the pK_{ROH} and the $FE^{o}_{Fc/Fc^+}(RO^{\bullet}/RO^{-})_{DMSO}$ data reported in the original literature. These relative values are claimed to be accurate to $\sim \pm 4$ kJ mol^{-1}.[43]



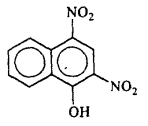
7 8 9

10

As discussed in Sec. 3, it is somewhat controversial to assign the values calculated from Eq. (21) to the gas phase. Bordwell and Liu[45] argued that the O–H bond dissociation enthalpy derived for phenol must be corrected for the difference between the enthalpies of solvation of PhOH and PhO$^{\bullet}$, but that no corrections are necessary for substituted phenols. In other words, the values derived from Eq. (21) should be referred to the gas phase. The option in the present review was, however, to consider those data as the solution phase bond dissociation enthalpies and tabulate them relative to the solution phase $D_{sln}(PhO-H) = 378.1$ kJ mol^{-1}.

Some of the results by Bordwell and co-workers[43,44,59] require supplementary information. First the oxidation potentials of some phenoxide ions were found to be reversible (2,4,6-tri-*tert*-butylphenol, 4-aminophenol, 4-methyl-2,6-di-*tert*-butylphenol, 4-ethyl-2,6-di-*tert*-butylphenol, 4-methoxy-2,6-di-*tert*-butylphenol, 2,4,6-tri-phenylphenol, 4-methylformyl-2,6-di-*tert*-butylphenol, and 4-nitro-2,6-di-*tert*-butylphenol), which lends further reliability to the respective O–H bond dissociation enthalpies in Table 4 [see, however, the discussion before Eq. (22)]. Second, the oxidation potential of the phenoxide ion derived from 3-hydroxyphenyl–methyl sulfone was measured in acetonitrile instead of dimethylsulphoxide. The corresponding value in Table 4 is therefore an approximation.

Zhao and Bordwell have recently reported new pK_{ROH} and $FE^{o}_{Fc/Fc^+}(RO^{\bullet}/RO^{-})_{DMSO}$ data for two substituted phenols,[60] from which additional O–H bond dissociation enthalpies could be calculated. One of them is the naphthol shown below (**11**) and the other is 4-chloro-2,6-dinitrophenol. The oxidation potentials of the phenoxide ions derived from 3-nitrophenol, 2,6-di-*tert*-butyl-4-nitrophenol, and 4-nitrophenol have also been reevaluated in the same paper and led to a significant change in $D_{sln}(O-H)$ in the case of the latter compound (Table 4).



11

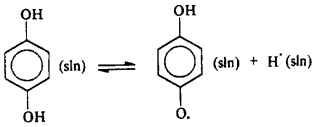
Equation (21) has also been used to calculate the O–H bond dissociation enthalpies from the data published by Arnett and co-workers for several substituted phenols.[50(a)] As pointed out in Sec. 3, although the oxidation potentials of the phenoxide ions in this paper are reversible, they were measured in a 5% solution of 3-methylsulfolane in sulfolane, whereas the pK_{RH} values were determined in dimethylsulphoxide. Therefore, although the error bars assigned to $D_{sln}(O-H)$ by Arnett *et al.* are small, varying between 1.1 and 1.8 kJ mol^{-1}, they should be considered low limits since they only reflect the uncertainties in the oxidation potentials. The results in Table 4 are anchored on $D_{sln}(PhO-H) = 383.4$ kJ mol^{-1} (Table 3).

The "gas phase" O–H bond dissociation enthalpies reported by Merényi and co-workers,[48(a)] displayed in Table 4, are relative to $D(PhO-H) = 356.4$ kJ mol^{-1} (Table 3) and rely on oxidation potentials of the phenoxide ions determined by equilibrium methods. As described in Sec. 3 for the case of phenol, those values were estimated by Eq. (20), using auxiliary data in the Appendix. It should be noted, however, that the calculation involves a somewhat controversial approximation: it has been assumed that the differences between the Gibbs energies of solvation of the substituted phenols and their phenoxy radicals are constant and equal to the value estimated for $\Delta_{sln}G(PhOH,g) - \Delta_{sln}G(PhO^{\bullet},g) = -12.6$ kJ mol^{-1}. The errors introduced by this assumption are difficult to assess, but should be no less than 5 kJ mol^{-1}. Another, probably less important approximation, was to identify the entropy term $T[S^{o}(R^{\bullet},g) - S^{o}(RH,g)]$ for all the substituted phenols with that for R=PhO. The uncertainties assigned by the authors vary between 1.3 and 5.9 kJ mol^{-1}, but they only reflect the

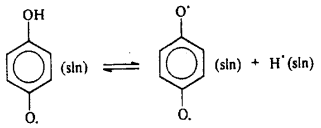
errors in the oxidation potentials of the phenoxide ions.

The pK_{RH}'s and oxidation potentials of R^- have also been used by Bausch and co-workers to probe the energetics of a variety of bonds in water and in dimethylsulphoxide.[61] As their values are relative to D_{sln}(N–H) in 1,4-dimethylurazole, the assumptions regarding the constant of Eq. (21) were no longer necessary. With regard to data for substituted phenols, the only O–H bond dissociation enthalpies reported by Bausch *et al.* are for phenol itself and for 4-chloro-2,6-dinitrophenol. The differences between these results, in both solvents, are shown in Table 4.

The last example involving the electrochemical methodology refers to the first and the second O–H bond dissociation enthalpies in *para*-hydroquinone [reactions (33) and (34)]. Friedrich used literature data for pK_{RH}'s and the oxidation potentials of the phenoxide ions in aqueous solution to derive the sum of the first two terms of Eq. (20) as 104.6 kJ mol^{-1} [reaction (33)] and 31.5 kJ mol^{-1} [reaction (34)].[62] If the last three terms of this equation are similar for both systems, then 104.6 − 31.5 = 73.1 kJ mol^{-1} represents the difference between the first and the second O–H bond dissociation enthalpies in *para*-hydroquinone (**12**). Absolute values of D(O–H) can be estimated under the reasonable assumption that the relevant auxiliary data given in the Appendix for phenol is valid for **12** and **13**. One obtains[49] D(O–H) = 327.7 and 254.6 kJ mol^{-1}, respectively.[63] The results displayed in Table 4 are relative to D(PhO–H) = 356.4 kJ mol^{-1} (Table 3).



12 13 (33)



(34)

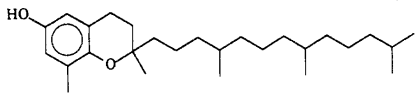
Parker, Cheng, and Handoo have also investigated the energetics of reactions (33) and (34) using the electrochemical method. They have obtained $\Delta_r G(33) = 328.4$ kJ mol^{-1} and $\Delta_r G(34) = 265.3$ kJ mol^{-1} in dimethylsulphoxide.[64] Assuming that $\Delta_r S(33) \approx \Delta_r S(34)$, 328.4 − 265.3 = 63.1 kJ mol^{-1} represents the difference between the first and the second O–H bond dissociation enthalpies in *para*-hydroquinone (**12**). If the solvation terms are similar in both reactions, then that difference applies also to the gas phase. Estimates of absolute D(O–H) values are more difficult than above. A lower limit of the first O–H bond dissociation enthalpy can be derived by using Eqs. (17)–(19) and data in the Appendix, together with 19.8 for the pK_a of *para*-hydroxybenzoquinone in DMSO and −0.247 V for the oxidation potential of the anion.[64] The calculation yields D_{sln}(O–H) > 348.7 kJ mol^{-1} and D(O–H) > 314.3 kJ mol^{-1},[65] in keeping with the value derived from Friedrich's experiments.

Photoacoustic calorimetry studies by Mulder, Saastad, and Griller[52] afforded O–H bond dissociation enthalpies in phenol and several substituted phenols. Although these early results were derived as described in Scheme 3, they were not corrected for the nonthermal expansion (see Sec. 3) and rely on some assumptions regarding solvation effects. Namely, $\Delta_r H(23)$ was obtained from Eq. (24) with $\Delta V/\chi = 0$. On the other hand, D_{sln}(O–H) were calculated with Eq. (36),[66] which was derived from Eq. (35) by canceling all the *solvation* enthalpies [note that this equation is mathematically equivalent to Eq. (25)] and using auxiliary data in the Appendix

$$D_{sln}(\text{O–H}) = \Delta_r H(23)/2 + \Delta_f H^\circ_m(\text{H}^\bullet,\text{g}) + \Delta_{sln} H(\text{H}^\bullet,\text{g}) + \Delta_f H^\circ_m(t\text{-BuOOBu-}t,\text{g})/2 - \Delta_f H^\circ_m(t\text{-BuOH,g}) + \Delta_{sln} H^\circ(t\text{-BuOOBu-}t,\text{g})/2 - \Delta_{sln} H^\circ(t\text{-BuOH,g}), \quad (35)$$

$$D_{sln}(\text{PhO–H}) = \Delta_r H(23)/2 + (359.8 \pm 1.4). \quad (36)$$

As observed in Eq. (35), the solvation terms are constant for all the phenols studied by Mulder, Saastad, and Griller. Ignoring them does not affect the accuracy of the relative data in Table 4 [absolute D_{sln}(O–H) values can be derived using D_{sln}(PhO–H) = 378.7 kJ mol^{-1}]. With respect to the nonthermal corrections, the errors in the relative bond dissociation enthalpies must be rather small, since it is fair to assume that the term $\Delta V/\chi$ is approximately constant for the different phenols. A small amendment has, however, been made in the original data by Mulder, Saastad, and Griller: they have used 0.85 for the quantum yield of the dissociation of di-*tert*-butylperoxide in benzene, whereas the presently accepted value is 0.83.[28] The enthalpy of reaction (23) was therefore recalculated with Eq. (24). It is finally noted that the authors claim ±2.1 kJ mol^{-1} for the relative accuracy of their data.

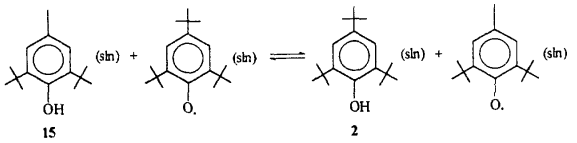


14

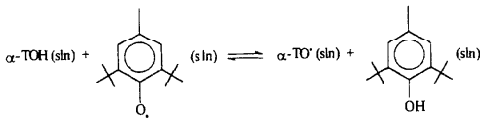
A recent PAC study by Wayner *et al.* reports O–H bond dissociation enthalpies for α-tocopherol (**10**), δ-tocopherol (**14**), and several other substituted phenols, in benzene and in the gas phase.[67] These data have been recalculated here by using the procedure described in Sec. 3 [Eqs. (27) and (28)]. The only modification refers to the solution terms in Eq. (28): supported by experimental results, Wayner and coworkers argued that those enthalpies nearly cancel each other (within less than ~±4 kJ mol^{-1}) for most of the substituted phenols involved in the present study.[68] Indeed, the ECW model predicts $\Delta_{sln} H(\text{PhOH,g}) - \Delta_{sln} H(\text{PhO}^\bullet,\text{g}) = -8.7$ kJ mol^{-1} in benzene (Table 3) and it is reasonable to expect values closer to zero for phenols which are much weaker acids than PhOH. This conclusion is also in keeping with the discussion by Bordwell and Liu,[45] referred to in Sec. 3. The

solution and the gas phase values displayed in Table 4 are relative to $D_{sln}(PhO-H)=378.7$ kJ mol^{-1} and $D(PhO-H)=365.0$ kJ mol^{-1} (Table 3). While the absolute uncertainties of the O–H bond dissociation enthalpies in solution are ~8–10 kJ mol^{-1}, the relative data in Table 4 are probably accurate to less than ±4 kJ mol^{-1}.

Other studies have addressed the energetics of the O–H bond in α-tocopherol, using different experimental approaches. In one of them, by Coronel and Colussi,[69] the equilibria (37) and (38) have been investigated in benzene, at 293 K, using ESR. The α-tocopherol is abbreviated by α-TOH. From the equilibrium constant of reaction (37) ($K=10.98$) and assuming a negligible entropy change, Coronel and Colussi obtained $\Delta_rH(37)=-5.8\pm0.3$ kJ mol^{-1}. This result, together with the O–H bond dissociation enthalpy in 2,4,6-tri-*tert*-butylphenol (334.1±1.3 kJ mol^{-1}; see Sec. 5), derived from the data by Mahoney, Ferris, and DaRooge,[33] leads to $D_{sln}(O-H)=328.3\pm1.3$ kJ mol^{-1} in 2,6-di-*tert*-butyl-4-methylphenol (**15**). This value was in turn used with the enthalpy of reaction (38), $\Delta_rH(38)=-16.1\pm0.3$ kJ mol^{-1}, to yield $D_{sln}(\alpha\text{-TO}-H)=312.2\pm1.4$ kJ mol^{-1}. As in the case of reaction (37), $\Delta_rH(38)$ was calculated from the equilibrium constant in benzene ($K=749$) and relies on the assumption of an insignificant entropy change.



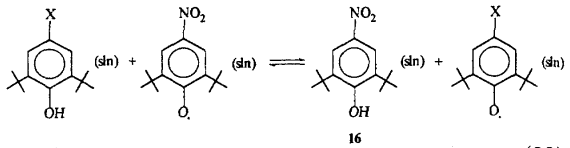
(37)



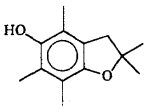
(38)

As noted in Sec. 5, the O–H bond dissociation enthalpy of 2,4,6-tri-*tert*-butylphenol is 4.1 kJ mol^{-1} higher in benzene than in chlorobenzene.[33] If the same difference is accepted for $D_{sln}(PhO-H)$, then the value 368.5 kJ mol^{-1} in chlorobenzene leads to $D_{sln}(PhO-H)=372.6$ kJ mol^{-1} in benzene. This was the anchor chosen to derive the relative data (Table 4) from the work by Coronel and Colussi.[69] It would probably be less correct to use the higher PAC value in benzene, $D_{sln}(PhO-H)=378.7$ kJ mol^{-1}, since those data rely on the results by Mahoney, Ferris, and DaRooge.[33]

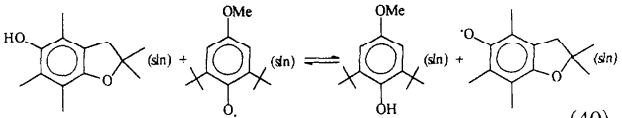
The same anchor, $D_{sln}(PhO-H)=372.6$ kJ mol^{-1} in benzene, was used to calculate the relative bond dissociation enthalpies (Table 4) from the equilibrium studies by Jackson and Hosseini.[70] These ESR studies were made in benzene and involved α-tocopherol and a number of substituted phenols. The equilibrium constants of reactions (39) were obtained at 294 K and afford the following reaction enthalpies (in kJ mol^{-1}, under the usual assumption that the entropy changes are negligible): −5.5 (X=CHO), −14.8 (X=CH_2NMe_2), −15.2 (X=Me), −15.6 (X=*t*-Bu, **2**), −20.3 (X=CHNOH), −29.0 (X=OMe), −26.5 (α-tocopherol, **10**), −31.5 (**17**). Using $\Delta_rH(39)=-15.6$ kJ mol^{-1} for X=*t*-Bu, together with $D_{sln}(O-H)=334.1\pm1.3$ kJ mol^{-1} in **2**, derived from Mahoney, Ferris, and DaRooge's data,[33] one obtains 349.7 kJ mol^{-1} for the O–H bond dissociation enthalpy in **16**. This value, in turn, allowed us to calculate the remaining bond dissociation enthalpies.



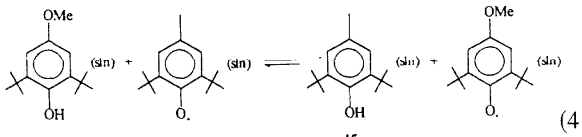
(39)



Equilibria (40) and (41) were also investigated in benzene, at several temperatures, by Jackson and Housseini. The van't Hoff plots led to $\Delta_rH(40)=3\pm3$ kJ mol^{-1} and $\Delta_rH(41)=-26\pm3$ kJ mol^{-1}, and to $\Delta_rS(40)=20\pm11$ J mol^{-1} K^{-1} and $\Delta_rS(41)=-42\pm11$ J mol^{-1} K^{-1}.[70] Although these fairly high entropies have been discussed by the authors, they were questioned by a careful study by Lucarini, Pedulli, and Cipollone,[71] where much lower values have been derived (see below), in keeping with our assumption in the previous paragraph. The data derived from the single temperature equilibrium constants was therefore preferred to calculate the relative values in Table 4. Be that as it may, it is instructive to compare the van't Hoff enthalpy values for reactions (40) and (41) with those derived above. Subtracting $\Delta_rH(39)=-15.2$ (X=Me) from $\Delta_rH(39)=-29.0$ kJ mol^{-1} (X=OMe), one obtains $\Delta_rH(41)=-13.8$ kJ mol^{-1}. The same exercise for X=OMe and **2** yields $\Delta_rH(40)=-2.5$ kJ mol^{-1}. Both values are of course at variance with those derived under the assumption of negligible entropy changes.



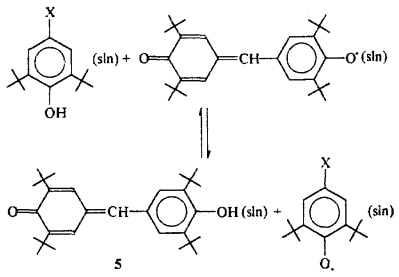
(40)



(41)

Another literature result for $\Delta_rH(41)$, −12.4±1.6 kJ mol^{-1}, reported by Coronel and Colussi,[72] has been obtained in a benzene–toluene mixture, through a van't Hoff plot in the temperature range of 251–304 K. The equilibrium constants have been determined by ESR spectroscopy. That value supports the option made in the previous paragraph (i.e., the preference by data derived from single temperature equilibrium constants), even considering that the reaction entropy derived by Coronel and Colussi, $\Delta_rS(41)=-18.5\pm5.6$ J mol^{-1} K^{-1},[72] is not that small. Van't Hoff

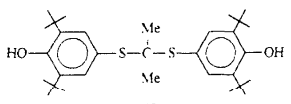
reaction entropies can be fairly unreliable, as indicated by the comparison between this result and the one quoted above, $\Delta_r S(41) = -42 \pm 11$ J mol^{-1} K^{-1}.[70]



5 (42)

Lucarini, Pedulli, and Cipollone have measured the equilibrium constants of reactions (42) in benzene or toluene, at 298 K or at several temperatures,[71] for X=OMe, Me, and *t*-Bu (**2**). For the *tert*-butyl substituent, the ESR studies in toluene (217–298 K range) led to $\Delta_r H(42) = 10.2 \pm 0.8$ kJ mol^{-1} and $\Delta_r S(42) = -3.0 \pm 2.6$ J mol^{-1} K^{-1}. The reaction enthalpy, together with the O–H bond dissociation enthalpy in 2,4,6-tri-*tert*-butylphenol (334.1 ± 1.3 kJ mol^{-1}; see Sec. 5), derived from the data by Mahoney, Ferris, and DaRooge,[33] yields $D_{sln}(O–H) = 323.9 \pm 1.5$ kJ mol^{-1} in **5**. This bond dissociation enthalpy can now be used to derive the remaining data. Whenever necessary, it was assumed that the reaction enthalpies are identical in benzene and in toluene. For X=OMe, $\Delta_r H(42) = -5.0 \pm 0.4$ kJ mol^{-1} and $\Delta_r S(42) = -6.9 \pm 1.5$ J mol^{-1} K^{-1} were obtained from measurements in toluene in the 232–327 K range, affording $D_{sln}(O–H) = 318.9 \pm 1.6$ kJ mol^{-1}. For X=Me, the equilibrium constant in benzene, at 298 K, gives $\Delta_r H(42) \approx \Delta_r G(42) = 8.0 \pm 0.2$ kJ mol^{-1} [73] and $D_{sln}(O–H) = 331.9 \pm 1.5$ kJ mol^{-1}.

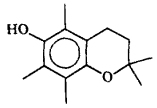
Lucarini, Pedulli, and Cipollone have also probed the energetics of the O–H bond in α-tocopherol (**10**) and probucol (**18**) by ESR equilibrium experiments in toluene.[71] The reactions were identical to (42) (i.e., hydrogen abstraction by the gavinoxyl radical, **5**) and the equilibrium constants at 298 K led to $\Delta_r H(42) \approx \Delta_r G(42) = 0.6 \pm 0.4$ kJ mol^{-1} (α-tocopherol) and $\Delta_r H(42) \approx \Delta_r G(42) = 9.3 \pm 0.5$ kJ mol^{-1} (probucol).[73] These values are consistent with $D_{sln}(O–H) = 324.5 \pm 1.6$ kJ mol^{-1} and $D_{sln}(O–H) = 333.2 \pm 1.6$ kJ mol^{-1}, respectively. All the O–H bond enthalpy data derived from the studies by Lucarini *et al.* were finally calculated relative to $D_{sln}(PhO–H) = 372.6$ kJ mol^{-1} in benzene (see above) and summarized in Table 4.



18

In a second paper by Lucarini *et al.*,[56] the O–H bond dissociation enthalpies of a variety of phenols (ArOH), including compounds **10** and **19**, have been determined in benzene, by the so-called "buffer method."[74] The method involved the ESR determination of equilibrium constants of reactions (43), where two phenols were in equilibrium with their phenoxy radicals. The production of these radicals was achieved by hydrogen abstraction with *t*-BuO˙, obtained by continuous photolysis of di-*tert*-butylperoxide.

$$ArOH(sln) + Ar'O^{\bullet}(sln) \leftrightharpoons ArO^{\bullet}(sln) + Ar'OH(sln) \quad (43)$$



19

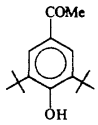
As in the case of phenol itself (see Sec. 3), the authors have anchored the $D_{sln}(O–H)$ values on the O–H bond dissociation enthalpy of 2,4,6-tri-*tert*-butylphenol, *in benzene*,[33] which was recalculated above as 334.1 ± 1.2 kJ mol^{-1}. Their results rely on the sensible assumption that the entropies of reactions (43) are negligible, so that $\Delta_r H(43) \approx \Delta_r G(43)$. Unfortunately, the experimental temperature is not indicated in the paper. The data in Table 4 assume that the experiments were made at 298 K and are relative to $D_{sln}(PhO–H) = 363.6 \pm 3.6$ kJ mol^{-1} (Table 3).

The energetics of O–H bonds in substituted phenols have also been investigated by several kinetic methods. In a study by Rousseau–Richard, Richard, and Martin,[75] the activation energies of reactions (44) in heptanol, determined in the temperature range 292–353 K, were used to derive $D_{sln}(O–H)$ relative to $D_{sln}(PhO–H)$. These values, displayed in Table 4, rely on a kinetic analysis of reaction (44) and are identified with the differences between the activation energy observed for each substituted phenol (ArOH) and for PhOH.

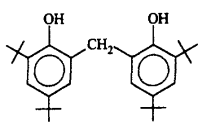
$$ArOH(sln) + (PhCO_2)_2(sln) \leftrightharpoons ArO^{\bullet}(sln) + PhCOO^{\bullet}(sln) + PhCOOH(sln). \quad (44)$$

Another set of relative data shown in Table 4 are based on the kinetic analysis of cross-disproportionation reactions involving several phenols, reported by Roginskii and Krasheninnikova.[76] The authors derived equilibrium constants of reactions (43), in benzene, at 323 K, from which the following $\Delta_r H(43)$ values can be calculated, under the assumption of negligible reaction entropies: −10.6 kJ mol^{-1} (ArOH=**19**, Ar'OH=**15**), 10.8 kJ mol^{-1} (ArOH=**2**, Ar'OH=**19**), 13.8 kJ mol^{-1} (ArOH=**20**, Ar'OH=**15**), −1.4 kJ mol^{-1} (ArOH=**21**, Ar'OH=**15**), and 1.5 kJ mol^{-1} (ArOH=**2**, Ar'OH=**15**). The last four reaction enthalpies, together with the O–H bond dissociation enthalpy in 2,4,6-tri-*tert*-butylphenol (**2**), 334.1 ± 1.3 kJ mol^{-1} (see Sec. 3), derived from the data by Mahoney, Ferris, and DaRooge,[33] yield $D_{sln}(O–H) = 332.6$ kJ mol^{-1} (in **15**), $D_{sln}(O–H) = 323.3$ kJ mol^{-1} (in **19**), $D_{sln}(O–H) = 346.4$ kJ mol^{-1} (in **20**), and $D_{sln}(O–H) = 331.2$ kJ mol^{-1} (in **21**). Note that the difference between the bond dissociation enthalpies for **15** and **19**, −9.3 kJ mol^{-1}, is reasonably consistent with the first of the reaction enthalpies given above, −10.6 kJ mol^{-1}. An additional test to these data, namely to the assumption that $\Delta_r S(43)$ is small, is provided by a van't Hoff value of $\Delta_r H(43)$, -13.2 ± 0.7 kJ mol^{-1}, also reported by Roginskii and Krasheninnikova, for ArOH=**19** and Ar'OH=**15**.[76]

This value, differs less than 4 kJ mol^{-1} from those obtained directly from the equilibrium constants.



20



21

It remains to be said that Roginskii and Krasheninnikova's data in Table 4 are relative to D_{sln}(PhO–H)=372.6 kJ mol^{-1}. As noted before, this anchor relies on D_{sln}(PhO–H)=368.5 kJ mol^{-1} in chlorobenzene, corrected for the difference (4.1 kJ mol^{-1}) between the O–H bond dissociation enthalpy of 2,4,6-tri-*tert*-butylphenol in benzene and in chlorobenzene.[33]

6. The O–H Bond Dissociation Enthalpies in Substituted Phenols: Gas-Phase Studies

Proton affinity values of substituted phenoxy radicals are rather scarce. A perusal of the *NIST WebBook*[3(a)] shows that the only data available are from a recent paper by Hoke *et al.*[19] Unfortunately, the application of Eq. (6) (see Sec. 2), to derive the corresponding O–H bond dissociation enthalpies is not possible, due to the lack of adiabatic ionization energy data. The only exception is 3-methylphenol. For this compound, the *NIST WebBook* recommends IE=799.9±1.9 kJ mol^{-1}, which, together with the proton affinity of the phenoxy radical, 877.5 kJ mol^{-1} [3(b),19] yields D(O–H)=365.4 kJ mol^{-1}. In Table 4, this value is displayed relative to D(PhO–H)=371.3 kJ mol^{-1}, recommended in Table 2.

Although gas-phase acidities [reaction (7)] of substituted phenols are more abundant[24] than proton affinities of phenoxy radicals, the use of Eq. (8) to calculate O–H bond dissociation enthalpies is hindered by the paucity of "independent" electron affinity values.[77] We were able to find the relevant data for only two compounds:[24] 3-fluorophenol ($\Delta_{acid}H$=1438.0±9 kJ mol^{-1}; EA=251.9±8.4 kJ mol^{-1}) and 2,3,5,6-tetrafluorophenol ($\Delta_{acid}H$=1431.3±19 kJ mol^{-1}; EA=265.7±8.4 kJ mol^{-1}). The corresponding bond dissociation enthalpies, 377.9±12.3 and 385.0±20.8 kJ mol^{-1}, are shown in Table 4 relative to D(PhO–H) =371.3 kJ mol^{-1}.

The gas-phase studies which have offered the most comprehensive view of substituent effects on O–H bond dissociation enthalpies in phenols, were those by Stein and co-workers.[15,78] With the very low pressure pyrolysis technique, the authors determined the activation energies of thermal decomposition reactions of a variety of substituted anisoles, XC_6H_4OMe, and related these data to the O–Me bond dissociation enthalpies. Stein and co-workers argued that, for the anisole series, D(O–Me)−D(PhO–Me) should be similar to D(O–H)−D(PhO–H) for the corresponding phenols. As they have noted, this assumption can be confirmed by the enthalpy of reaction (45), which can be expressed in terms of the above differences [Eq. (46)]

$$XC_6H_4OMe(g)+PhOH(g)\rightarrow XC_6H_4OH(g)+PhOMe(g), \quad (45)$$

$$\Delta_rH(45)=\Delta D_{anisoles}-\Delta D_{phenols}. \quad (46)$$

While the standard enthalpies of formation for the substances involved in reaction (45) are only available for a very limited number of X, the group contribution scheme[12] shows that, in fact, $\Delta_rH(45)$ must be zero, in the absence of considerable specific interactions in *ortho* and *meta* compounds. Recent density functional theory calculations by Wu and Lai also indicate that the substituent effects on the O–H and O–Me bond dissociation enthalpies in phenol and anisole are almost identical.[79] It was under this transferability assumption that the relative O–H bond dissociation enthalpies displayed in Table 4 were derived.

7. The O–H Bond Dissociation Enthalpies in Substituted Phenols: Computational Chemistry Studies

As stated in Sec. 1, the main purpose of this paper is to provide a comprehensive and critical survey of *experimental* data for O–H bond dissociation enthalpies in phenol and substituted phenols. However, it was deemed useful to include the results of several theoretical studies, not only for the sake of completeness but mainly because those studies gave a rather important contribution to our understanding of substituent effects. Moreover, such insights are also relevant to discuss empirical estimation methods.

We are aware of four publications where computational chemistry was used to investigate the thermochemistry of O–H bonds in substituted phenols. The relative bond dissociation enthalpies obtained in those studies, for the compounds which were also probed by experimental techniques, are displayed in Table 4.[80]

In the oldest of the papers containing theoretical results, by Suryan, Kafafi, and Stein,[78] semiempirical AM1 calculations were used and the authors claimed an average deviation of ~6 kJ mol^{-1} from the experimental values. They have also acknowledged that this "error" may obscure some interesting trends. A higher level of calculation [B3LYP density functional with a modified 6-31G(,p) basis set] was used by Wright *et al.* to calculate single point energies of a variety of phenols and phenoxy radicals, whose geometries and vibration frequencies were obtained by the AM1 method.[81] The error due to this procedure, i.e., using the AM1 geometries instead of those obtained from B3LYP/6-31(,p), was estimated from the results for phenol and phenoxy radical as ~3 kJ mol^{-1} and applied to correct the remaining values. Finally, several approximations have also been used to derive the data at 298 K. Although no average error is indicated in this work, the reliability of the relative trend is probably better than 8 kJ mol^{-1}.

Interestingly, the O–H bond dissociation enthalpy calculated for phenol by Wright *et al.*, 361.7 kJ mol^{-1}, is in better agreement with the value recommended in Table 2, D(PhO–H) = 371.3 ± 2.3 kJ mol^{-1}, than data computed at higher levels of theory by Brinck, Haeberlein, and Jonsson.[82] The only exception was the result afforded by the single point MP4/6-31(d) calculation using a MP2/6-31(d) geometry, which is only 6 kJ mol^{-1} higher than our selected value. The B3LYP/6-31(d,p) method, used for geometry optimization and energetics, gave an O–H bond dissociation enthalpy 28 kJ mol^{-1} lower than the recommended value in Table 2. Despite these discrepancies, it is noted that the relative ΔD(O–H) data for two substituents (4-NH_2 and 4-NO_2), calculated with both of the above theory levels, are similar (within ~5 kJ mol^{-1}). The B3LYP/6-31(d,p) method was therefore chosen by the authors to evaluate the relative O–H bond dissociation enthalpies in several monosubstituted phenols.[82]

The fourth theoretical paper, by Wu and Lai, reports the energetics of O–H and O–Me bonds in substituted phenols, investigated by two different density functional methodologies.[79] One is a local density approximation method with a double numerical basis set for geometry optimization (JMW/DN). The other is the nonlocal BLYP method with a 6-31G(d) basis set. Those methods led to the following O–H bond dissociation enthalpy values in phenol: 367.4 and 314.2 kJ mol^{-1}, respectively. Although the former result is much closer to the selected D(PhO–H) = 371.3 ± 2.3 kJ mol^{-1} (Table 2) than the BLYP calculation, when both series of theoretical ΔD(O–H) values are compared (Table 4) it is observed that the methods yield data which seldom differ by more than ~5 kJ mol^{-1}— only the values for 4-NH_2 and 4-NMe_2 disagree by more than 12 kJ mol^{-1}. Nevertheless, a significant discrepancy is noted when the computed results for D(PhO–H) − D(PhO–Me) are compared with the experimental values: the JMW/DN and the BLYP/6-31G(d) calculations yield 65.7 and 75.3 kJ mol^{-1}, respectively, whereas the data in the Appendix give 99.5 ± 1.6 kJ mol^{-1}. It must be stressed that this experimental difference is equal to the enthalpy of reaction (47) and therefore does not rely on the thermochemistry of the phenoxy radical.

$$\mathrm{PhOH(g) + Me^{\bullet}(g) \rightarrow PhOMe(g) + H^{\bullet}(g)}. \qquad (47)$$

8. The O–H Bond Dissociation Enthalpies in Substituted Phenols: Recommended Data

We are now better equipped to select data in Table 4. It is recognized that this exercise may be controversial, particularly where large discrepancies exist. Furthermore, the publication of new theoretical and experimental data will probably invalidate some of the selections. Yet, the choices are necessary at this stage in order to assess our present understanding of the substituent effects on the O–H bond dissociation enthalpies in phenols.

TABLE 5. Values of the O–H bond dissociation enthalpies (T = 298 K) in monosubstituted phenols, relative to D(PhO–H). Selected data (kJ mol^{-1})

Substituent	ΔD(O–H)[a]	σ[b]	σ^+[c]	σ^-[d]
2-Me	−9 ± 4			
3-Me	−3 ± 4	−0.07	−0.10[e]	
4-Me	−8 ± 4	−0.17	−0.31	−0.17
2-$CHCH_2$	−10 ± 8			
4-*t*-Bu	−7 ± 4	−0.20	−0.26	−0.13
4-Ph	−12 ± 4	−0.01	−0.18	0.02
4-O^-	−68 ± 8	(−0.81)	−2.30	−0.82
4-$O^{\bullet}$	−102 ± 13			
2-OH	−30 ± 8			
3-OH	1 ± 8	0.12	(0.05)	
4-OH	−27 ± 10	−0.37	−0.92	−0.37
2-OMe	−17 ± 4			
3-OMe	0 ± 4	0.12	0.05[e]	
4-OMe	−22 ± 4	−0.27	−0.78	−0.26
2-CH_2OH	−10 ± 8			
2-COMe	−6 ± 8			
3-COMe	5 ± 4	0.38	(0.38)	
4-COMe	9 ± 5	0.50		0.84
3-COEt	9 ± 10	0.38	(0.38)	
4-COPh	11 ± 10	0.43	0.51	0.83
4-CO_2^-	7 ± 10	0.00	−0.02	0.31
4-OCOMe	−11 ± 10	0.31	−0.19	
3-COOEt	7 ± 8	0.37	0.37[e]	
2-NH_2	−31 ± 10			
3-NH_2	−5 ± 4	−0.16	−0.16[e]	
4-NH_2	−40 ± 13	−0.66	−1.30	−0.15
3-NMe_2	−8 ± 10	−0.16	(−0.16)	
4-NMe_2	−50 ± 10	−0.83	−1.70	−0.12
2 CN	0 ± 8			
3-CN	13 ± 8	0.56	0.56[e]	
4-CN	18 ± 8	0.66	0.66	1.00
2-NO_2	−5 ± 8			
3-NO_2	19 ± 8	0.71	0.73[e]	
4-NO_2	25 ± 8	0.78	0.79	1.27
4-CH_2CHNH_2COOH	−7 ± 8			
2-F	−8 ± 8			
3-F	6 ± 8	0.34	0.35[e]	
4-F	−4 ± 4	0.06	−0.07	−0.03
2-Cl	−3 ± 4			
3-Cl	5 ± 4	0.37	0.40[e]	
4-Cl	−1 ± 4	0.23	0.11	0.19
2-Br	−7 ± 8			
4-Br	2 ± 4	0.23	0.15	0.25
4-I	−1 ± 10	0.18	0.14	0.27
3-CF_3	13 ± 4	0.43	0.57[e]	
4-CF_3	17 ± 4	0.54	0.61	0.65
3-SO_2Me	11 ± 8	0.60	(0.60)	
4-SO_2Me	22 ± 8	0.72		1.13

[a]Selected data from Table 4.
[b]σ_p or σ_m. Data quoted from Ref. 91. Estimated values are in parentheses.
[c]σ_p^+ or σ_m^+. Data quoted from Ref. 91, unless stated otherwise. Estimated values in parentheses.
[d]σ_p^- or σ_m^-. Data quoted from Ref. 91.
[e]Data quoted from Ref. 90.

The criteria to derive the recommended values in Table 4 (also summarized in Table 5) were, in most cases, straightforward. Simple or weighed averages of experimental data, often seasoned with the most reliable computational results, were commonly used (we have resisted the temptation to "adjust" the selections according to the discussion and the

empirical correlations examined in Sec. 9). There is, however, a general assumption which must be stated. It is observed in Table 4 that gas phase and solution data are often similar within ~5 kJ mol^{-1}— a difference which is lower than the usual uncertainties affecting both the experimental and computational results. Therefore, in order to select the "best" data, it seemed sensible to consider that most of the experimental values in Table 4, which have been derived from solution studies, also apply to the gas phase. Exceptions to this guideline, and also to the criteria mentioned above, are readily apparent and will be discussed below. Finally, with regard to the uncertainties assigned to the selections, it should be mentioned that they have been chosen not only on the basis of the spread of the results but also on the reliability of the experimental methods.

The largest difference between experimental and calculated results in Table 4 refers to 4-O^-. Wu and Lai attributed the ~75 kJ mol^{-1} discrepancy to the solvation effects induced by that substituent [see Eq. (13)], which is a very good electron donor.[79] This is, at first sight, surprising, since one would expect similar solvation enthalpies for the parent phenol and its radical. It could be argued that the basis set used by the authors, which does not contain diffuse functions, is not suitable to investigate the energetics of anions. However, recent calculations made with a better basis set, including those functions, essentially confirm the result obtained by Wu and Lai.[83]

Computational and experimental data in the cases of *ortho*- and *para*-aminophenol are also at variance. For the 2-NH_2 isomer the only available experimental result,[78] -31 ± 10 kJ mol^{-1}, has been recommended but, noting the theoretical values and also the data for the *para* isomer, the selection may well be an upper limit. Indeed the VLPP result for *para*-aminophenol is ~40 kJ mol^{-1} higher than the two other values derived from the electrochemical studies,[43,48(a)] the computational numbers lying in between. The recommended value in Table 4, -40 ± 13 kJ mol^{-1}, may also be an upper limit.

9. Discussion of Substituent Effects on O–H Bond Dissociation Enthalpy: Empirical Correlations and Estimation Methods

The substituent effects on the thermodynamic stability of the O–H bond in phenolic compounds can be evaluated from the ΔD(O–H) data summarized in Table 5. Recall that each of those values represents the enthalpy of reaction (48), which measures the difference between the O–H bond dissociation enthalpies in the substituted phenol (ArOH) and in phenol (PhOH). Positive and negative ΔD(O–H) indicate, respectively, that the bond is stabilized and destabilized, compared to the O–H bond in phenol

$$\mathrm{ArOH(g)+PhO^{\bullet}(g)\rightarrow ArO^{\bullet}(g)+PhOH(g).} \quad (48)$$

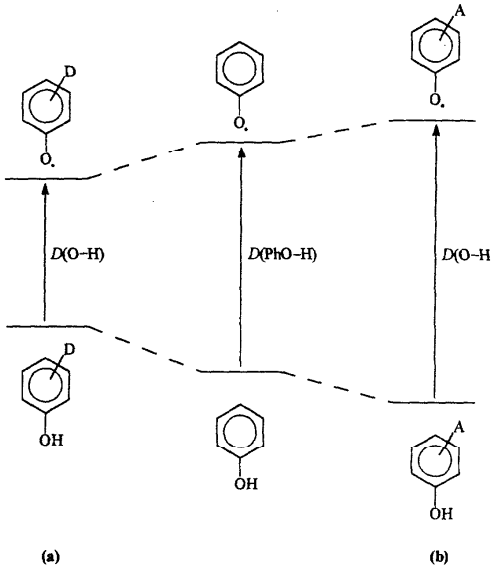


FIG. 1. Schematic effect of an electron donor (D) and acceptor (A) substituent on the O–H bond dissociation enthalpy. Adapted from Ref. 79.

Discussions of the substituent effects on ΔD(O–H) and correlation of these differences with other substituent parameters are abundant in the chemical literature.[30,33,43,44,48(a),52,56,67,71,78,79,81,82,84–87] At first sight, from a thermodynamic point of view, it seems sensible to explain the variation in ΔD(O–H) in terms of stabilization or destabilization of the substituted phenol, ArOH, and its phenoxy radical, ArO$^{\bullet}$, relative to PhOH and PhO$^{\bullet}$, respectively (the substituent effect on the stability of ArOH will henceforth be called *parent contribution* and that related to the radical fragment will be designated by *radical contribution*[88]). Figure 1 illustrates these ideas for two possibilities: (a) stabilization of the radical and destabilization of ArOH and (b) stabilization of ArOH and destabilization of the radical. The first case implies ΔD(O–H) < 0 and the second leads to ΔD(O–H) > 0. Apparently, there is nothing wrong with this approach, since is deals with experimentally determined quantities (bond dissociation enthalpies) and it basically conveys the same information as in Table 5. Yet, Fig. 1 contains additional facts. Note, for instance in case (a), that the ground state of the phenol with a D substituent is represented *above* the ground state of PhOH and the ground state of the radical is *below* the ground state of PhO$^{\bullet}$. When it is suggested, as in Fig. 1(a), that the molecule DC_6H_4OH is destabilized relative to phenol, which data are used to substantiate that claim? Certainly not the standard enthalpy of formation. For example, in the case of D=4-OH, $\Delta_f H^{\circ}_m$[1,4-$(HO)_2C_6H_4$,g] $= -265.3$ kJ mol^{-1} is far more negative than $\Delta_f H^{\circ}_m(C_6H_5OH,g) = -96.4$ kJ mol^{-1}.[2] Nevertheless, as seen in Table 5, 1,4-benzenediol has a O–H bond dissociation enthalpy which is 27 kJ mol^{-1} smaller than D(PhO–H). Following this line of reasoning, the lower O–H bond dissociation enthalpy in the diol and its much lower enthalpy of formation will then imply that PhO$^{\bullet}$ is

more stabilized by the additional *para*-OH group than PhOH. Seemingly, there is no problem with this interpretation. It is simply a new situation, not covered by Fig. 1: both species (parent and radical) are stabilized by the D group but to different extents. However, one should keep in mind that (by definition) it is meaningless to compare enthalpies of formation (or total electronic energies, for that matter) of molecules with a different number of atoms.

The point made in the previous paragraph is trivial, but it was deemed appropriate to recall that *thermodynamic stability* is a frequently misused concept. While it is legitimate to state that a given species is stabilized, for instance, by changing its structure or bonding, it is misleading to state that the same species will be stabilized by adding a substituent group. The new species will obviously have a different energy since it contains more atoms. It is therefore believed that attempts to draw schemes like the one in Fig. 1 lack physical significance. Nevertheless, as illustrated below, if used with caution, they are certainly helpful in visualizing substituent effects.

9.1. Monosubstituted Phenols

Despite being difficult, or even impossible, to discriminate between parent and radical contributions, the final outcome is available directly from bond dissociation enthalpy data. ΔD(O–H) results in Table 5 measure the net substituent effects on the thermodynamic stability of the *same* bond. Let us start the discussion with the phenols which have a single substituent at the *para* position.

The ΔD(O–H) values for *para* monosubstituted phenols spread over a wide range, from -68 kJ mol^{-1} (4-O$^-$) to 25 kJ mol^{-1} (4-NO$_2$), in contrast, for example, with the much narrower variation observed for C–H bonds in several families of compounds.[86] The strong substituent effect in the case of phenols has been attributed to the high polarity of the O–H bond[52] (also see below). Mulder, Saastad, and Griller have proposed a correlation between D(O–H) and the modified Hammett parameter σ^+.[52] This was preferred to the most common σ scale, since it accounts for through conjugation effects, which will be important for electron-donor groups, such as 4-Me, 4-OH, 4-OMe, 4-O$^-$, 4-NH$_2$, and 4-NMe$_2$.[89,90] Indeed, as observed in Table 5, where values for σ and σ^+ have been collected,[91] those groups have the largest $\sigma_p^- - \sigma_p$ differences. The linear plot suggested by Mulder, Saastad, and Griller involved only four points besides phenol (4-CF$_3$, 4-Cl, 4-*t*-Bu, and 4-OMe) and was questioned by Stein, Kafafi, and Suryan who tested it by using their own VLPP data (Table 4).[78] However, much better correlations were later found by Lind *et al.*[48(a)] and by Jonsson *et al.*[84] As remarked by Stein's group, the physical meaning of these correlations is not obvious. Moreover, the selection of the σ_p^- data set is also important.[92] In order to try the method with the selected ΔD(O–H) values in Table 5, we have used the parameters recommended by Hansch, Leo, and Taft.[91] As shown by Fig. 2 and Eq. (49), the correlation (r=0.991) is excellent—the slope and intercept error bars

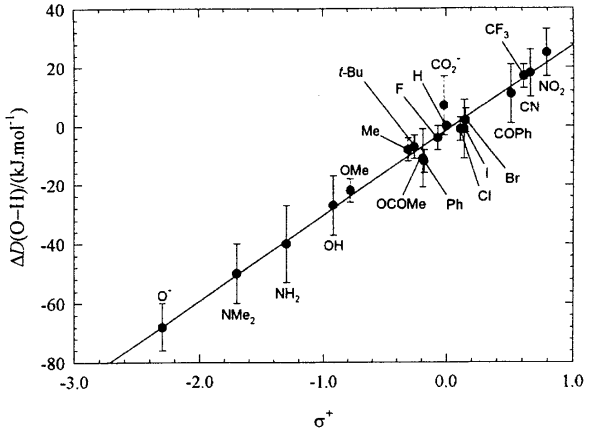


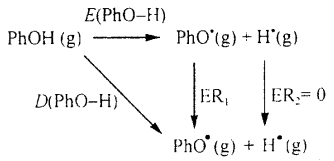
FIG. 2. O–H bond dissociation enthalpies for *para* monosubstituted phenols, relative to D(PhO–H), plotted against σ^+. The least squares line is given by Eq. (49).

are fortuitously much better than the uncertainties assigned to the individual relative bond dissociation enthalpies

$$\Delta D(\text{O–H}) = (28.95 \pm 0.95)\sigma_p^+ - (1.29 \pm 0.80). \quad (49)$$

Equation (49) can thus be used to predict new ΔD(O–H) data for *para* monosubstituted phenols. It is concluded either from this equation or from Fig. 2 that *para* electron donating groups ($\sigma_p^+ < 0$) lead to a decrease of the phenolic O–H bond dissociation enthalpy, whereas electron withdrawing *para* substituents ($\sigma_p^+ > 0$) yield higher bond dissociation enthalpies. In fact, similar results led Bordwell and co-workers to argue that the "O–H bond is weakened by increasing the electron density within the bond and strengthened by decreasing the electron density within the bond."[86] This is, perhaps, surprising: as remarked by Brinck *et al.*, theoretical studies show that an electron density increase in the bonding region is followed by an increase in bond strength.[82] We can attempt to reconcile these ideas by recalling that *bond strength* and *bond dissociation enthalpy* are not synonyms. Scheme 4 and Eq. (50) show the differences for the case of phenol. The starred fragments indicate that these species have the same structure as in the parent compound. Therefore, E(PhO–H), called the *bond enthalpy term*, should be regarded as a "bond-snap" enthalpy, which is related to D(PhO–H) by the *relaxation* or *reorganization energies*, ER_1 and ER_2. Only ER_1 matters in the example, since the hydrogen atom has no relaxation energy

$$D(\text{PhO–H}) = E(\text{PhO–H}) + ER_1. \quad (50)$$



Scheme 4

Similar schemes have been used in the literature to discuss the systematics of several bonds.[93] The usefulness of Scheme

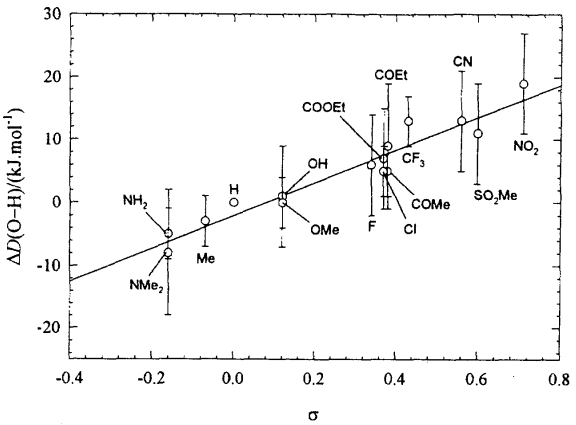


FIG. 3. O–H bond dissociation enthalpies for *meta* monosubstituted phenols, relative to D(PhO–H), plotted against σ. The least squares line is given by Eq. (51).

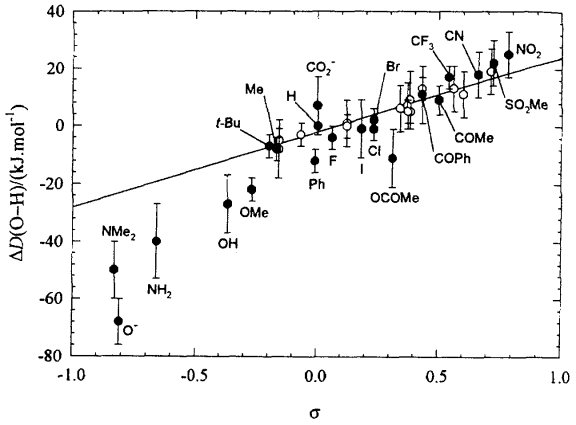


FIG. 4. O–H bond dissociation enthalpies for *para* (filled circles) and *meta* (open circles) monosubstituted phenols, relative to D(PhO–H), plotted against σ. The line has been defined with the data for the *meta* groups [Eq. (51)].

4 in the present context is to stress that the trend defined by the bond terms E(O–H) may not parallel the trend observed for D(O–H). In other words, the bond terms, which will be closer to the *bond strength* concept since they do not include the relaxation of the fragment radicals to their ground states, may indeed increase (relative to the bond term in phenol) with electron donor substituents, in keeping with the theoretical studies. Nevertheless, the same substituents may also lead to much more exothermic relaxations than PhO*, so that the net result is a decrease in D(O–H). Although the calculation of quantities like ER_1 can be readily made with computational chemistry methods, no data are yet available for phenolic compounds. It must be added, however, that the recent studies by Brinck and co-workers indicate that the O–H bond properties are not affected by the nature of the substituents, the stabilizing effects being attributed to "their ability to delocalize the oxygen lone pair." [82] This suggests that the observed trend is due not to different E(O–H) values but rather to the effect of the substituent on the stabilization of the molecule as a whole.

As mentioned above, recently several groups have made attempts to understand the trend of O–H bond dissociation enthalpies in substituted phenols by discussing the stability of the radicals and their parent compounds. The experimental approach followed by Bordwell and co-workers was based in a plot where D(O–H) in *para* and *meta* monosubstituted phenols were represented against the Hammett parameter σ.[44,86] As evidenced by Fig. 3, obtained from the data selected in Table 5 and from the σ_m parameters tabulated by Hansch, Leo, and Taft,[91] the relative O–H bond dissociation enthalpies in the *meta*-substituted compounds follow a reasonable linear variation [Eq. (51); $r=0.96$] with those parameters

$$\Delta D(\mathrm{O–H}) = (26.07 \pm 2.01)\sigma_m - (2.07 \pm 0.76). \quad (51)$$

Following Bordwell *et al.*,[44,86] when the data for the *para*-substituted compounds (Table 5) are plotted in the same graph as the *meta* compounds (Fig. 4), it is noted that, in general, the electron-withdrawing and the weakly electron-donating *para* substituents fall in the *meta* line.

Before drawing any conclusions from Figs. 3 and 4, it is appropriate to recall briefly some basic textbook ideas about electronic substituent effects.[89,90] In the absence of electron delocalization, only the total *inductive effect*, which reflects the electron polarization of a bond, is operative. This effect can be assessed by the Hammett parameter at the *meta* positions. Substituents which occupy the *para* (and *ortho*) position, on the other hand, also may have the possibility of interacting with the aromatic ring by *resonance effects*. As these effects are not significant at the *meta* positions,[94] the difference $\sigma_p - \sigma_m$ will measure the resonance effect. It is of course assumed that the inductive/field effect has the same intensity in the *para* and *meta* positions.

According to the previous ideas, the fact that the *meta* line is approximately followed by some *para* substituents in Fig. 4 indicates that in these cases the resonance effects are very small. This has been acknowledged by Bordwell and co-workers, who have also noted (see Fig. 4) that the points for strong electron donors deviate from the *meta* line, defining another line with a higher slope.[44,86] The explanation of this trend raised some controversy. Bordwell and Cheng[43] argued that "effects of remote substituents on the ground state of parent molecules will be small compared to those on radicals." The conclusion that the O–H bond dissociation enthalpies are only determined by radical stabilization were questioned by Clark and Wayner.[95] Their photoacoustic calorimetry studies led to the conclusion that C–Br bond dissociation enthalpies in a series of *para*-substituted benzyl bromides, $4\text{-}XC_6H_4CH_2Br$, decreases with electron withdrawing substituents, whereas it was known that the C–H bond in *para*-substituted toluenes, $4\text{-}XC_6H_4Me$, varies in the opposite direction. Given the fact that in both homolytic processes the same radicals ($4\text{-}XC_6H_4CH_2^{\bullet}$) are formed, the contrasting variation in the bond dissociation enthalpies must be due to a (de)stabilization of the parent

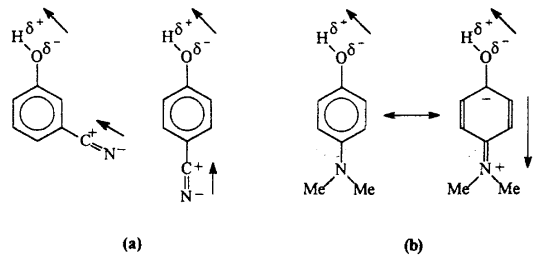


FIG. 5. Dipolar interaction in the cases of (a) an electron-withdrawing and (b) an electron–donor substituent. Adapted from Ref. 86.

compounds.[95] This view was accepted by Bordwell's group to account for the data that fit the *meta* line: *meta* and *para* electron acceptors lead to positive ΔD(O–H) values because they stabilize the parent phenolic compound. As displayed in Fig. 5 (taken from the work by Bordwell *et al.*[86]) the dipole associated with the O–H bond has a stabilizing interaction with the C≡N bond dipole. Figure 5 also shows that the same rationale can be used to explain the negative ΔD(O–H) values for electron donors. In the case of dimethylamine phenol, the dipoles have a repulsive interaction, implying a destabilization of the compound.

The results by Clark and Wayner mentioned above[95] have been recently questioned by Mulder and co-workers,[96] who found no change in C–Br bond dissociation enthalpies in several *para*-substituted benzyl bromides. We believe, however, that the dipole interaction hypothesis remains a useful reasoning, although it is not entirely clear, after the above discussion on stability, what authors mean by "stabilization of the compound." The same doubt applies to the explanation advanced by Bordwell *et al.* to account for the negative ΔD(O–H) values for strong electron donors (Fig. 4). They have argued that the lower bond dissociation enthalpies in these cases are due primarily to the stabilization of the radicals by delocalization of the odd electron, rather than to parent phenol destabilization (Fig. 5).[86] In fact in the case of the arylacetonitrile family $XC_6H_4CH_2CN$ for example, a plot of the C–H bond dissociation enthalpies versus σ shows behavior similar to Fig. 4. Namely, the ratios between the slope of the line defined by the *para* electron donors and the slope of the *meta* line are rather close.[86] As the C–H dipole is small compared to that of the O–H bond, the dipole interaction of Fig. 5 can hardly explain the trend observed for the electron donors in the arylacetonitrile family. Therefore, according to Bordwell and co-workers, the ΔD(C–H) and the ΔD(O–H) data will, in these cases, measure the radical stabilization energies. Or, in other words, the low bond dissociation enthalpies in phenols containing electron-donating *para* substituents is due essentially to radical contributions.

While the work by Bordwell *et al.* provides an elaborate justification for the data in Fig. 4, it is recalled that Hammett plots are of difficult interpretation and it is not always clear why linear relationships should be observed. Incidentally, when the σ^- scale is used, a fairly good correlation [Eq. (52); $r=0.990$] involving the selected data (Table 5) for *meta* and *para* substituents is observed in Fig. 6

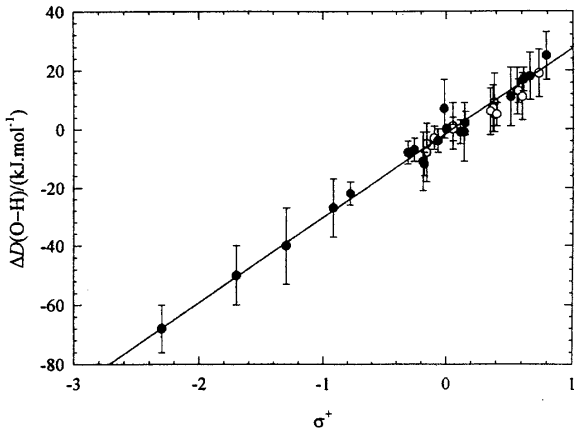


FIG. 6. O–H bond dissociation enthalpies for *para* (filled circles) and *meta* (open circles) monosubstituted phenols, relative to D(PhO–H), plotted against σ^+. The line is the best fit of all data [Eq. (52)].

$$\Delta D(\text{O–H}) = (28.13 \pm 0.74)\sigma^+ - (2.08 \pm 0.51). \quad (52)$$

It is interesting to point out that the success of the correlations in Figs. 2 and 6 is consistent with the conclusion that radical stabilization energies are the dominating terms in the case of electron–donor groups. As evidenced in Table 5, the σ^+ values for these substituents are significantly more negative than the corresponding σ parameters, indicating (or accounting for) an increased conjugation effect.

The method outlined in Scheme 4 would probably be a valid alternative to investigate the origin of ΔD(O–H) trends, but as the information required is not available, let us now look at other alternatives, discussed by Wu and Lai[79] and by Brinck, Haeberlein, and Jonsson.[82]

Using density functional theory calculations (see Sec. 7), Wu and Lai derived the energies of isodesmic reactions (53) and (54) for a variety of X.[79] According to these authors, these energies reflect, respectively, the parent and the radical contributions. The difference $\Delta_r H(53) - \Delta_r H(54) = \Delta_r H(48)$, is identified with ΔD(O–H).


(53)


(54)

What does a negative value of $\Delta_r H(53)$ indicate? Simply that the traditional bond additivity schemes,[12,97,98] which would estimate 0 kJ mol^{-1}, fail to reproduce that value, either because the reactants are more unstable than predicted or because the products are more stable. Assigning the net effect only to the phenolic compounds is forgetting the changes in the other two molecules. So, reaction (53) cannot be regarded as an *accurate* measure of the parent effect. Let us accept, however, that the approximation holds. Then $\Delta_r H(53) < 0$ will imply that the substituted phenol is destabilized relative to PhOH and therefore the parent contri-

TABLE 6. Parent (PC), radical (RC), and total (TC) contributions to ΔD(O–H) in monosubstituted phenols (T=298 K). Data in kJ mol^{-1}

Substituent	PC[a]	PC[b]	RC[a]	RC[b]	RC[c]	TC[a]	TC[b]	ΔD(O–H)[d]
4-Me	2	2	−6	−7	−1	−8	−9	−8±4
4-OH	9	2	−17	−17	−15	−26	−19	−27±10
4-OMe	7	3	−18	−18	−13	−25	−21	−22±4
4-NH_2	3	6	−35	−30	−21	−38	−36	−40±13
4-NMe_2	8	7	−35	−34	−26	−43	−41	−50±10
4-NO_2	−6	−18	11	0	7	17	18	25±8
4-F	6		−4		−3	−10		−4±4
3-Cl		−7		0	−3		7	5±4
4-Cl	2	−7	−2	−8	−5	−4	−1	−1±4
4-CN	−4	−15	4	−9	3	8	6	18±8
4-Br	3[e]		−3[e]		−2	−6[e]		2±4
4-COMe	−6		2		−2	8		9±5
4-CF_3	−2	−10	8	3	5	10	13	17±4
4-SO_2Me	−4		11		5	15		22±8
4-O^-	16		−122		−45	−138		−68±8

[a]Data calculated with the BLYP/6-31G(d) method, by Wu and Lai (Ref. 79), unless noted otherwise.
[b]Data calculated with the B3LYP/6-31(d,p) method, by Brinck, Haeberlein, and Jonsson (Ref. 82).
[c]Data calculated with the method by Bordwell and co-workers (Ref. 86): differences between the ΔD(O–H) values calculated with Eq. (51) and the corresponding selected experimental values (last column).
[d]Selected ΔD(O–H) values from Table 5.
[e]Data calculated with he JMW/DN method, by Wu and Lai (Ref. 79).

bution will be positive—it increases the energy of 4-XC_6H_4OH [see Fig. 1(a)]. The opposite conclusion is of course drawn when $\Delta_r H(53)$ is positive [Fig. 1(b)].

A similar discussion can be made about the enthalpy of Eq. (54) and its identification with the radical contribution. Once again, if this is accepted, then for example $\Delta_r H(54) > 0$ will imply that the substituted phenoxy radical is stabilized relative to PhO$^\bullet$, so that the radical contribution will be negative—it decreases the energy of 4-$XC_6H_4O^\bullet$ [see Fig. 1(a)]. The opposite conclusion is drawn when $\Delta_r H(54)$ is negative [Fig. 1(b)].

The parent and radical contributions reported by Brinck, Haeberlein, and Jonsson[82] were determined by using a different approach, although they also rely on density functional theory calculations (see Sec. 7). In order to probe the parent contributions in several monosubstituted phenols, the authors calculated the spacial minima in the electrostatic potential associated with the oxygen, relative to phenol (ΔV_{min}), and plotted the results against ΔD(O–H). Noting that this potential had been used to study inductive and resonance effects in other aromatic systems, Brinck and co-workers found that ΔV_{min} increases linearly with ΔD(O–H) for electron-withdrawing substituents. However, ΔD(O–H) for electron-donating groups show a much smaller variation with ΔV_{min}. These observations indicate, therefore, that parent contributions have a dominant weight in the O–H bond dissociation enthalpies for electron-acceptor groups, but are of minor importance in the case of electron-donor substituents. As stressed by the authors, the conclusion is in keeping with the one reached by Bordwell's group[86] (see above).

The radical contribution was assessed by calculating the surface maxima in the spin density associated with the oxygen of the substituted phenols and the results expressed relative to the value for PhOH ($\Delta\rho^S_{max}$). By plotting these data against ΔD(O–H), Brinck *et al.* found that only the molecules with electron donors defined a linear correlation [ΔD(O–H) increases with $\Delta\rho^S_{max}$], indicating that the radical contribution is of major importance in these cases.[82] The bond dissociation enthalpies for phenols with electron-acceptor groups vary little with $\Delta\rho^S_{max}$ and do not exhibit any trend.

Brinck and co-workers evaluated the parent and the radical contributions by introducing the parameters ΔV_{min} and $\Delta\rho^S_{max}$ in Eq. (55) and, using their computed ΔD(O–H) data, were able to derive the constants a and b. The first term in this equation was identified with the relative destabilization energy of the parent phenol and the second with the relative stabilization energy of the radical.[82] In the nomenclature used in the present review, the parent contribution will be given by $-a\Delta V_{min}$ and the radical contribution by $b\Delta\rho^S_{max}$

$$\Delta D(\text{O–H}) = a\Delta V_{min} + b\Delta\rho^S_{max}. \quad (55)$$

Parent contributions (PC), radical contributions (RC), and total contributions (TC=RC−PC) calculated by Wu and Lai[79] and by Brinck, Haeberlein, and Jonsson[82] are displayed in Table 6, together with the RC data afforded by Bordwell's method, described above. The selected experimental values of ΔD(O–H) (Table 5) were also included for comparison. It is observed, with regard to parent contributions (first two columns), that the Wu and Lai's method usually yields the highest values, i.e., the parent phenolic compound is either more destabilized or less stabilized than that predicted by Brinck and co-workers. The agreement between the data sets is reasonable, but still not satisfactory, since we are probing fairly small effects. The same comments apply to the results shown in the third and fourth columns, which refer to the radical contributions. Keeping in mind that the empirical

method proposed by Bordwell's group relies on an approximate linear correlation, the RC values in column six are in general closer to the theoretical results than might be anticipated.

Although the fine detail might be lost by inaccuracies of the PC and RC values in Table 6, it is still possible to recognize some useful patterns: (1) PC is negative for electron–acceptor substituents (implying stabilization of the parent phenolic compound) and positive for electron–donor groups (destabilizing the parent compound); (2) RC can be negative for both types of substituents (stabilizing the phenoxy radical), but the effect is much larger for strong electron donors; (3) For strong electron donors the TC is dominated by the RC values. It is finally noted that there is fairly good agreement between the TC data (with the conspicuous exception, 4-O^-, mentioned above) and the selected experimental values of ΔD(O–H).

Let us now discuss O–H bond dissociation enthalpies in *ortho* monosubstituted phenols. The available data (Table 5) indicate that all substituents in this position destabilize the phenolic bond. Even electron–acceptor groups such as NO_2 and CN, which stabilize the O–H bond in the *meta* and *para* positions, lead to $\Delta D(\text{O–H}) \leq 0$.

The most simple explanation of the *ortho*-weakening effect is the existence of a repulsive steric interaction between the two neighboring groups, which is relieved upon cleavage of the O–H bond. However, another effect, acting in the opposite direction, may be operative. Some substituents containing heteroatoms like oxygen or nitrogen stabilize the parent phenol compound by forming a hydrogen bond and have a positive contribution on ΔD(O–H).[81] Table 4 contains information that illustrates both situations. For instance, the computational results by Wright *et al.* (see Sec. 7) show that the O–H bond dissociation enthalpy in 2-methylphenol varies by 4 kJ mol^{-1} when the hydroxyl bond changes its orientation relative to the methyl group. The "toward" conformer, where the hydroxyl bond points toward the substituent, is destabilized relative to the "away" conformer, which has no repulsive interaction between the two groups.[99] Note also that the existence of repulsive interaction in the *ortho* isomer is consistent with the experimental ΔD(O–H) values, selected in Table 4, for the 2- and 4-methylphenol, the former being more negative. A dramatic example of the importance of the hydrogen bond is provided by the "away" and "toward" conformers of 2-methoxyphenol: the O–H bond dissociation enthalpy is 24 kJ mol^{-1} higher in the latter. Moreover, according with the computational results in Table 4 and as expected, ΔD(O–H) for the "away" 2-methoxyphenol is identical to ΔD(O–H) for 4-methoxyphenol phenol. Therefore, as stressed by Wright *et al.*, the strong hydrogen bond is responsible for the stabilization of the "toward" conformer.

The ΔD(O–H) data selected (Table 4) for 1,2- and 1,4-dihydroxybenzene are identical when the uncertainties are considered, although, after the results by Stein *et al.*,[78] it may well be possible that the value for the *ortho* compound is significantly lower than ΔD(O–H) for the *para* compound.

TABLE 7. Substituent effects on the O–H bond dissociation enthalpies (T=298 K) in disubstituted phenols, relative to D(PhO–H). Data in kJ mol^{-1}

Substituents	ΔD(O–H)[a]	ΔD_1(O–H)[b]	ΔD_2(O–H)[c]
2,6-Me_2	−14±4	−9	−5
3,5-Me_2	−3±4	−3	0
2,4-t-Bu_2	−22±8	−7[d]	−15[e]
2,6-t-Bu_2	−26±8	−15[f]	−11
3,5-t-Bu_2	−6±4	−5[g]	−1
2,6-Ph_2	−11[h]		
2,6-$(OMe)_2$	−21±8	−17	−4
3,5-$(OMe)_2$	−7±8	0	−7
2,6-$(NO_2)_2$	26[i]	−5	31
2,6-Cl_2	−1[j]	−3	2
3,5-Cl_2	14±4	5	9

[a]Selected data from Table 4.
[b]Contribution of the first substituent to ΔD(O–H). Data from Table 5, except when noted otherwise.
[c]Contribution of the second substituent to ΔD(O–H). ΔD_2(O–H) $=\Delta D$(O–H)$-\Delta D_1$(O–H).
[d]Contribution from the *tert*-butyl group at the *para* position.
[e]Contribution from the *tert*-butyl group at the *ortho* position.
[f]Value derived from the data for 2,4-t-Bu_2.
[g]Estimated with Eq. (51).
[h]Calculated from the selected values for 2,4,6-Ph_3 and 4-Ph (Table 4).
[i]Calculated from the selected values for 2,6-$(NO_2)_2$-4-Cl and 4-Cl (Table 4).
[j]Calculated from the selected values for 2,4,6-Cl_3 and 4-Cl (Table 4).

This situation would contrast with the one discussed above for the methoxy substituent and would imply that any stabilization of the parent *ortho* compound would be offset by a large stabilization of the corresponding phenoxy radical, presumably due to the formation of a strong hydrogen bond.[78,81] The same comments and conclusion are appropriate for the results for 2- and 4-aminophenol. It is noted that the calculated ΔD(O–H) values for the *ortho* isomer are indeed more negative than for the *para* isomer. It is plausible that both the hydrogen bond stabilization of the 2-aminophenoxy radical and a destabilizing steric interaction in the parent phenol contribute to the observed trend.

In summary, *ortho* substituents which are hydrogen acceptors may increase the O–H bond dissociation enthalpy by stabilizing the parent phenol. *Ortho* substituents which are hydrogen donors may lead to a decrease in D(O–H) due to the stabilization of the radical.

9.2. Di- and Trisubstituted Phenols

Can we use the experimental results for monosubstituted phenols and the conclusions above to understand and to predict O–H bond dissociation enthalpies for di- and trisubstituted phenols? The most simple starting point is to consider that substitutent effects are approximately additive and use the selected experimental data for mono- and disubstituted phenols to evaluate the contribution of the first and the second substituent. The results of this useful exercise, previously made by Lucarini *et al.*[56] and by Wright *et al.*,[81] are presented in Table 7.

Keeping in mind the error bars affecting the experimental ΔD(O–H) results, most values in Table 7 can be explained easily. For instance, the steric repulsion between the OH group and the adjacent *tert*-butyl substituent, destabilizing the parent phenol, leads to a significant decrease in ΔD_1(O–H). The effect of two of these substituents, as observed for 2,6-*t*-Bu_2, is comparable for the first and the second. Nevertheless, if the error bars are overlooked, it is somewhat surprising that the effect of the first *tert*-butyl group is more destabilizing for the O–H bond than the second. With a single *ortho* alkyl substituent the O–H bond can move to the "away" position, in order to minimize the repulsion, but when the second bulky group is added there is no such possibility. Therefore, the relationship ΔD_1(O–H) $>\Delta D_2$(O–H) [or $|\Delta D_1(\text{O–H})|<|\Delta D_2(\text{O–H})|$] could be anticipated. The same comments apply to the data for 2,6-Me_2, where it is also observed that the first *ortho* methyl substituent yields a slightly more negative contribution than the second.

The largest $\Delta D_1(\text{O–H})-\Delta D_2(\text{O–H})$ differences in Table 7 are for 2,6-$(OMe)_2$ and 2,6-$(NO_2)_2$. In the case of the methoxy compound, the larger effect of the first substituent may reflect the fact that the O–H bond is "away" from OMe, while this bond will be constrained to the "toward" configuration when the second methoxy is in place. This will stabilize the molecule through an intramolecular hydrogen bond, leading to a less negative contribution to ΔD(O–H). While this explanation looks sensible, why does the molecule 2-$MeOC_6H_4OH$ take the less stable (away) configuration? Maybe it does not and the trend results from the stability of the 2-$MeOC_6H_4O^{\bullet}$ and 2,6-$(MeO)_2C_6H_3O^{\bullet}$ radicals: the first methoxy substituent, which leads to a fairly high stabilization energy of the radical (Table 6), may also cause a "saturation" phenomenon, i.e., the introduction of the second methoxy group will have a much smaller electron delocalization effect and a smaller contribution to the relaxation energy. This explanation can be checked if ΔD(O–H) for 2,4-$(MeO)_2C_6H_3OH$ becomes available.

The very large difference in the case of the nitro substituents, particularly the negative value observed for the first substituent, is hardly justifiable. NO_2 is a strong electron acceptor, thus increasing the O–H bond dissociation enthalpy. The formation of a hydrogen bond would enhance this effect, since it would stabilize the parent molecule. As it is difficult to conceive that steric interactions are such that make $\Delta D_1(\text{O–H})<0$, the problem may be in the VLPP result for 2-NO_2. This is, in fact, suggested by the AM1 calculation (Table 4), which gives $\Delta D_1(\text{O–H})=10.9$ kJ mol^{-1}.

Additivity rules and the data in Tables 5 and 7 were applied in Table 8 to calculate ΔD(O–H) in trisubstituted phenols. These values were then compared with the experimental results. It is seen that most differences $\Delta D(\text{O–H})_{exp}-\Delta D(\text{O–H})_{calc}$ are smaller or close to the experimental uncertainties. Some, however, deserve additional comment. The experimental value for 2,6-*t*-Bu_2–4-Et, for example, which is 7 kJ mol^{-1} smaller than the calculated, is also smaller (by 11 kJ mol^{-1}) than $\Delta D(\text{O–H})_{exp}$ for 2,6-*t*-Bu_2–4-Me. Accepting that the latter is correct, a quick look to the data for both compounds in Table 4 will show that the selected value for 2,6-*t*-Bu_2–4-Et must be ~10 kJ mol^{-1} too negative. In fact, it can be expected that the effects of *para* methyl and ethyl substituents are similar.

The next conspicuous discrepancy in Table 8 refers to 2,6-*t*-Bu_2–4-CHO. Although $\Delta D(\text{O–H})_{calc}$ relies on an es-

TABLE 8. Substituent effects on the O–H bond dissociation enthalpies ($T=298$ K) in polysubstituted phenols, relative to D(PhO–H). Data (in kJ mol^{-1}) calculated by the "group additivity method"

Substituents	$\Delta D(\text{O–H})_{exp}$[a]	$\Delta D(\text{O–H})_{calc}$[b]	Difference[c]
Trisubstituted phenols			
2,4,6-Me_3	−23±4	−22	−1
2,6-*t*-Bu_2-4-Me	−32±8	−34	2
2,6-*t*-Bu_2-4-Et	−43±10	−36[d]	−7
2,4,6-*t*-Bu_3	−37±4	−33	−4
2,4,6-Ph_3	−23±10		
2,6-*t*-Bu_2-4-CHO	−28±8	−17[e]	−11
2,6-Me_2-4-OMe	−42±8	−36	−6
2,6-*t*-Bu_2-4-OMe	−45±4	−48	3
2,6-*t*-Bu_2-4-O-*t*-Bu	−49±8	−48[f]	−1
2,6-*t*-Bu_2-4-COMe	−26±8	−17	−9
2,6-*t*-Bu_2-4-OCOMe	−26±10	−37	11
2,6-*t*-Bu_2-4-CH_2NMe_2	−38±8		
2,4,6-$(OMe)_3$	−35±8	−43	8
2,6-Me_2-4-NO_2	0±10	11	−11
2,6-*t*-Bu_2-4-NO_2	−19±4	−1	−18
2,6-*t*-Bu_2-4-CHNOH	−43±8	−26[g]	−17
2,4,6-Cl_3	−2±8	−7	5
3,4,5-Cl_3	13±10	16	−3
2,6-$(NO_2)_2$-4-Cl	25±8	25	0
Other phenols			
2,3,6-Me_3-4-OMe	−38±8	−39	1
2,3,5,6-Me_4-4-OMe	−27±8	−42	15
2,3,5,6-F_4	14±8	−6	20
F_5	−11±8	−10	−1
1-naphthol (**7**)	−25±4	h	
2-naphthol (**8**)	−8±4	h	
5	−47±4	h	
6	−49±8	h	
17	−54±8	h	
19	−44±8	−42	−2
21	−41±8	h	
α-tocopherol (**10**)	−43±4	−42	−1
δ-tocopherol (**14**)	−29±8	−28	−1
probucol (**18**)	−39±8	−45[h]	6
2,4-dinitro-1-naphthol (**11**)	5±10	11[i]	−6
2-OH-6-Br-naphthalene (**9**)	−6±10	−6[j]	0

[a]Selected data from Table 4.
[b]Calculated on the assumption of additivity of substituent effects. Data from Tables 5 and 7.
[c]$\Delta D(\text{O–H})_{exp}-\Delta D(\text{O–H})_{calc}$.
[d]The contribution of the 4-Et substituent, −10 kJ mol^{-1}, was estimated with Eq. (49).
[e]The contribution of the 4-CHO substituent, 9 kJ mol^{-1}, was estimated with Eq. (51).
[f]Assuming that the contribution of 4-O-*t*-Bu is similar to OMe.
[g]The contribution of the 4-CHNOH substituent, 0 kJ mol^{-1}, was estimated with Eq. (51).
[h]See discussion in Sec. 9.3.
[i]Estimate based on $\Delta D(\text{O–H})_{exp}$ for 1-naphthol.
[j]Estimate based on $\Delta D(\text{O–H})_{exp}$ for 2 naphthol.

timate for the contribution of the *para*-acyl group and this is somewhat uncertain,[100] this is probably not the only cause for the apparent additivity failure. The difference is more likely due to the experimental value for this compound. In fact, it is observed in Table 4 that the data obtained by Jackson and Hosseini[70] are consistently 4–8 kJ mol^{-1} more negative than the selected data (see also the discussion in Sec. 5), which suggests that $\Delta D(\text{O–H})_{\text{exp}} = -28$ kJ mol^{-1} in Table 8 may be too low. This may also occur for the experimental values of 2,6-*t*-Bu$_2$–4-CHNOH and 2,6-*t*-Bu$_2$–4-COMe.

The only large positive $\Delta D(\text{O–H})_{\text{exp}} - \Delta D(\text{O–H})_{\text{calc}}$ value in Table 8 for trisubstituted phenols respects to 2,6-*t*-Bu$_2$–4-OCOMe. We suspect that $\Delta D(\text{O–H})_{\text{calc}}$ is in error in this case, since it was derived from a single experimental result for $\Delta D(\text{O–H})$ in *para*-acetylphenol and this value relies on the assumption, mentioned in Sec. 5, that the pK_a of phenol in sulfolane is close to the value measured in dimethylsulfoxide.[50(a)] While this approximation leads to some data in fair agreement with selections in Table 4, the values for the substituents 4-Me, 4-CN, and 4-NO$_2$ are ~11–16 kJ mol^{-1} too low. If a deviation of similar magnitude occurs for 4-OCOMe, then the correct $\Delta D(\text{O–H})_{\text{calc}}$ in Table 8 will be much closer to $\Delta D(\text{O–H})_{\text{exp}}$. This possibility is supported by the correlations in Figs. 2 and 4, where the points for OCOMe lie below the lines.

There is no obvious reason to suspect the experimental values for 2,6-Me$_2$–4-NO$_2$ and 2,6-*t*-Bu$_2$–4-NO$_2$ in Table 8. So either the additivity fails in these cases (particularly for the latter compound—note the error bars), or the terms to calculate $\Delta D(\text{O–H})_{\text{calc}}$ are unreliable. As $\Delta D(\text{O–H})_{\text{calc}}$ for 2,4,6-Me$_3$ and 2,6-*t*-Bu$_2$–4-Me are in very good agreement with the experimental values (Table 8), the contributions of 2,6-Me$_2$ and 2,6-*t*-Bu$_2$ should be trusted. Therefore, the problem (if any) must lie on the selection for $\Delta D(\text{O–H})$ in *para*-nitrophenol. In fact, the data available for this compound in Table 4 and also the correlations in Figs. 2 and 4 suggest that the selected value may be too high.

A probably fortuitous observation about the largest $\Delta D(\text{O–H})_{\text{exp}} - \Delta D(\text{O–H})_{\text{calc}}$ values for trisubstituted phenols—but still worth mentioning—comes to mind. With the obvious exception of 2,6-*t*-Bu$_2$–4-Et, whose experimental value is clearly inconsistent with other selected data, the discrepancies in Table 8 occur for electron–donor substituents. Should they be attributed to the causes discussed above or will those groups produce some breakdown of additivity?

9.3. Polysubstituted Phenols

We can now apply the additivity assumptions to polysubstituted phenols. The results obtained for $\Delta D(\text{O–H})_{\text{calc}}$, as well as the differences $\Delta D(\text{O–H})_{\text{exp}} - \Delta D(\text{O–H})_{\text{calc}}$ are displayed in Table 8.

The first significant discrepancy between $\Delta D(\text{O–H})_{\text{exp}}$ and $\Delta D(\text{O–H})_{\text{calc}}$ is noted for 2,3,5,6-Me$_4$–4-OMe. The contributions of 2,6-Me$_2$ (−14 kJ mol^{-1}), 3,5-Me$_2$ (−3 kJ mol^{-1}), and 4-OMe (−22 kJ mol^{-1}) lead to $\Delta D(\text{O–H})_{\text{calc}} = -42$ kJ mol^{-1}, which is 15 kJ mol^{-1} more negative than $\Delta D(\text{O–H})_{\text{exp}}$. This difference can be understood on the following grounds. The *para*-methoxy group is forced out of the aromatic plane due to a steric interaction with the two *meta*-methyl substituents.[101] Therefore, its ability to stabilize the radical is affected substantially, because the conjugation between the oxygen and the ring is reduced.[56,81] As the contributions used to derive $\Delta D(\text{O–H})_{\text{calc}}$ do not include this steric constraint, it is not surprising that a positive difference is observed in Table 8. It must be stressed that only the OMe group—and not the OH group—is driven out of the ring plane. It has been shown by Wright *et al.* that even when two bulky substituents like *tert*-butyl groups are *ortho* to OH, the O–C(sp^2) bond remains in the aromatic plane.[81]

The attention is now turned to α-tocopherol (**10**). It is noted that $\Delta D(\text{O–H})_{\text{exp}}$ is in excellent agreement with $\Delta D(\text{O–H})_{\text{calc}}$ obtained above for 2,3,5,6-Me$_4$–4-OMe. In fact, the chromanol configuration is such that it forces the O–C(sp^2) bond to be more planar with the ring, allowing a more "normal" conjugation effect.[85,101] In the case of δ-tocopherol (**14**), lacking the two *ortho*-methyl groups (which contributed with −14 kJ mol^{-1}), $\Delta D(\text{O–H})_{\text{calc}} = -28$ kJ mol^{-1} is also very close to $\Delta D(\text{O–H})_{\text{exp}}$.

The "net" chromanol contribution to $\Delta D(\text{O–H})$ in α-tocopherol can be evaluated as −26 kJ mol^{-1} by using $\Delta D(\text{O–H})_{\text{exp}} = -43$ kJ mol^{-1} and subtracting the contributions of 2,6-Me$_2$ (−14 kJ mol^{-1}) and 3-Me (−3 kJ mol^{-1}). A similar calculation can be made to derive −37 kJ mol^{-1} as the contribution of the furane ring in **17**. This more negative value is in keeping with the fact that the C(sp^2)–O bond is even more planar with the aromatic ring than in the case of α-tocopherol.[101]

Although the additivity method cannot be applied to several compounds in Table 8, due to insufficient information, it is still possible to use $\Delta D(\text{O–H})_{\text{exp}}$ data to draw some useful conclusions. For instance, a very crude $\Delta D(\text{O–H})_{\text{calc}}$ value for the diphenol **21** can be obtained as −31 kJ mol^{-1} by adding the contributions of 2,4-*t*-Bu$_2$ (−22 kJ mol^{-1}) and 2-Me groups (−9 kJ mol^{-1}). A slightly smaller value (−34 kJ mol^{-1}) is predicted if 2,4,6-*t*-Bu$_3$ is used as a model. The fact that the experimental result is more negative is seemingly the result of stronger steric interactions by the benzylic group, which destabilize the parent phenol. Two other very negative values of $\Delta D(\text{O–H})_{\text{exp}}$ in Table 8 are for compounds **5** and **6**. In both cases the *para* substituents are electron donors. Therefore, according with the discussion above [see also Figs. 1 and 5(b)], one can expect a destabilization of the parent molecules. However, this effect must be small compared with the large (exothermic) radical relaxation energies. Of course, the steric relief upon cleavage of the O–H, due to the adjacent *tert*-butyl groups, also contributes to the decrease in bond dissociation enthalpy. The final example in the series is probucol (**18**), a molecule where two *ortho tert*-butyl substituents are also present. $\Delta D(\text{O–H})_{\text{calc}}$ can be roughly evaluated as −45 kJ mol^{-1} by using the contribu-

tions of 2,6-t-Bu_2 (-26 kJ mol^{-1}) and 4-SMe (-19 kJ mol^{-1}).[102]

The results for the naphtholic compounds in Table 8 also provide interesting questions and insights. $\Delta D(O-H)_{exp}$ for 1-naphthol (**7**) is 17 kJ mol^{-1} lower than for 2-naphthol (**8**). Stein and co-workers have attributed this difference to the greater stabilization of 1-naphthoxy radical.[78] Bordwell and Cheng remark that the radical stabilizations should be comparable but the ground state of 1-naphthol may be slightly higher.[43] Computational chemistry studies may shed some light on this unsettled issue. Better understood is the value for $\Delta D(O-H)_{exp}$ in 2-OH-6-Br-naphthalene. The contribution of a para-bromo group is 2 kJ mol^{-1}—the exact difference between the O–H bond dissociation enthalpies in this compound and in 2-naphthol. The prediction of $\Delta D(O-H)_{exp}$ in 2,4-dinitro-1-naphthol (**11**) is also fairly consistent, particularly bearing in mind the problem (discussed above) about the contribution of 2-NO_2. Accepting the value derived from the AM1 calculations, 11 kJ mol^{-1}, and using 25 kJ mol^{-1} for the contribution of 4-NO_2, the O–H bond dissociation enthalpy in the dinitro compound is estimated to be 11 kJ mol^{-1} higher than in 1-naphthol.

Let us finish this detailed discussion on both a negative and a positive note. One of the largest discrepancies (20 kJ mol^{-1}) between $\Delta D(O-H)_{exp}$ and $\Delta D(O-H)_{calc}$ in Table 8 is for 2,3,5,6-F_4. One may question the calculated value, which was obtained by adding the contributions of 2-F (-8 kJ mol^{-1}) and 3-F (5 kJ mol^{-1}) substituents, but when these values, together with the contribution of 4-F (-4 kJ mol^{-1}), are used to evaluate $\Delta D(O-H)_{calc}$ in F_5, the final result, -10 kJ mol^{-1}, is very close to $\Delta D(O-H)_{exp}$ in the pentafluoro phenol. This casts some doubts on the reliability of the experimental result for the O–H bond dissociation enthalpy in the tetrafluoro compound (see, however, below).

9.4. Additivity of Hammett Parameters

There is another, more indirect, way to test the additivity of substituent effects. The method, which has been applied by Jonsson *et al.*[84] and by others[67,81] to predict the net result of several substituents on the O–H bond dissociation enthalpy, involves the use of a correlation between $\Delta D(O-H)$ and σ^- for *ortho* (σ_o^-), *meta* (σ_m^-) and *para* (σ_p^-) groups. It has already been shown in Fig. 6 and Eq. (52) that *meta* and *para* substituents follow a rather good linear relationship. However, due to the irregular interactions between *ortho* substituents and the OH group, it is somewhat controversial, assigning σ^- values to them. The approach followed by Jonsson and co-workers is simple: they have considered $\sigma_o^- = a\sigma_p^-$, where a is a constant, and eliminated from the plot groups that imply strong steric interactions, such as t-Bu. Based on the ratio of the slopes of the correlations involving $\Delta D(O-H)_{para}$ vs σ_p^- and $\Delta D(O-H)_{ortho}$ vs σ_p^-, those authors recommend $a = 0.66$.[84] Their exercise was repeated here with the data selected in Table 5 for the mono-substituted *ortho* phenols and σ_p^+, leading to Eq. (56) ($r = 0.929$). This correlation, together with Eq. (49), affords $a = 17.88/28.95 = 0.62$.[103]

$$\Delta D(O-H) = (17.88 \pm 2.69)\sigma_p^+ - (6.78 \pm 1.73). \quad (56)$$

The main point of Eq. (56) is to show that it is possible to extend the correlation in Fig. 6 to data for some *ortho* substituents. The value of the empirical constant a, which is used to estimate σ_o^+ from tabulated σ_p^+ values, is less important.[104] In fact, using all the available data in Table 5 for *ortho*, *meta*, and *para* substituents,[103] we have tested the method for $a = 0.66$, and $a = 0.62$. As observed in Eqs. (57) and (58), the differences are small.[105] The best correlation appears to be that for $a = 0.66$ and we have decided to use this value in subsequent predictions. Naturally, this conclusion may change with the availability of more accurate $\Delta D(O-H)$ results.

$a = 0.66$:

$$\Delta D(O-H) = (28.31 \pm 0.91)\sigma^+ - (3.11 \pm 0.59) \quad (r = 0.980) \quad (57)$$

$a = 0.62$:

$$\Delta D(O-H) = (28.44 \pm 0.93)\sigma^+ - (3.18 \pm 0.60) \quad (r = 0.980). \quad (58)$$

The application of Eq. (57) to di- and polysubstituted phenols is illustrated in Table 9. Each σ^+ value was obtained by adding σ_o^+ ($= 0.66\sigma_p^+$), σ_m^+, and σ_p^+ for all substituents. It is noted that the overall agreement with experimental $\Delta D(O-H)$ values is fair, but worse than in Table 8, where the "group additivity scheme" was used. In addition, σ^+ parameters are not available for many important groups. However, in cases where there is not enough information to use the additivity scheme (as for 2,4,6-Ph_3), the "generalized" Hammett plot is a useful way of estimating data.

An interesting point in Table 9 regards the differences between $\Delta D(O-H)_{exp}$ and $\Delta D(O-H)_{calc}$ for 2,3,5,6-F_4 and for F_5. In contrast to the results in Table 8, the agreement is now bad for the latter and excellent for the former. Hence, the above remark on the unreliability of $\Delta D(O-H)_{exp}$ for the tetrafluorophenol may be questionable. The only safe conclusion is that the two values are probably inconsistent. There is also a simple—but important—lesson from this example: assessing experimental data with empirical correlations may lead to erroneous conclusions.

9.5. Other Correlations

For the sake of completeness, two other methods that have been used to estimate O–H bond dissociation enthalpies in substituted phenols are finally mentioned. One has been applied by several groups (see, e.g., Refs. 52, 56, 85, and 87) and involves correlations of $D(O-H)$ with rate constants of reactions where the phenoxy radicals are produced. Implicit in these relationships is the assumption of constant activation entropies. The second empirical estimation procedure is due to Denisov and involves the application of a "parabolic"

TABLE 9. Substituent effects on the O–H bond dissociation enthalpies ($T=298$ K) in polysubstituted phenols, relative to D(PhO–H). Data (in kJ mol^{-1}) calculated by the "generalized Hammet plot"

Substituents	$\Delta D(\text{O–H})_{\text{exp}}$[a]	$\Delta D(\text{O–H})_{\text{calc}}$[b]	Difference[c]
Disubstituted phenols			
2,6-Me_2	−14±4	−15	−1
3,5-Me_2	−3±4	−9	6
3,5-*t*-Bu_2	−6±4	−7	1
2,6-Ph_2	−11[d]	−10	−1
2,6-$(OMe)_2$	−21±8	−32	11
3,5-$(OMe)_2$	−7±8	0	−7
2,6-$(NO_2)_2$	26[e]	26	0
2,6-Cl_2	−1[f]	1	−2
3,5-Cl_2	14±4	19	−5
Trisubstituted phenols			
2,4,6-Me_3	−23±4	−24	1
2,4,6-Ph_3	23±10	15	8
2,6-Me_2-4-OMe	−42±8	−37	−5
2,4,6-$(OMe)_3$	−35±8	−54	19
2,6-Me_2-4-NO_2	0±10	8	−8
2,4,6-Cl_3	−2±8	4	−6
3,4,5-Cl_3	13±10	23	−10
2,6-$(NO_2)_2$-4-Cl	25±8	29	−4
Other phenols			
2,3,6-Me_3-4-OMe	−38±8	−40	2
2,3,5,6-Me_4-4-OMe	−27±8	−42	15
2,3,5,6-F_4	14±8	14	0
F5	−11±8	12	−22

[a]Selected data from Table 4.
[b]Calculated with Eq. (57). σ^+ was obtained in each case by adding σ_o^+, σ_m^+, and σ_p^+ for all substituents ($\sigma_o^+=0.66\sigma_p^+$). Data from Tables 5 and 7.
[c]$\Delta D(\text{O–H})_{\text{exp}}-\Delta D(\text{O–H})_{\text{calc}}$.
[d]Calculated from the selected values for 2,4,6-Ph_3 and 4-Ph (Table 4).
[e]Calculated from the selected values for 2,6-$(NO_2)_2$–4-Cl and 4-Cl (Table 4).
[f]Calculated from the selected values for 2,4,6-Cl_3 and 4-Cl (Table 4).

model.[106–108] The agreement between his results and the selected data in the present paper is generally fair.

10. Conclusions

Despite the considerable number of experimental and theoretical studies involving the thermochemistry of the O–H bond in phenolic compounds, there are still fundamental issues which remain to be ascertained. The values of many bond dissociation enthalpies need either to be confirmed or to be determined more accurately, allowing more rigorous tests for prediction methods and providing a better understanding of substituent effects. These effects on D(O–H) are often small and the uncertainties assigned to most of the data presently available probably hinder interesting trends. Perhaps the most relevant knowledge to be gained in future studies concerns the solvation of phenoxy radicals. This is, in fact, one of the main sources of uncertainty in the experimental results. Information on solvation energetics requires values of O–H bond dissociation enthalpies in the gas phase and in solution, but while the latter are relatively abundant, the former are still very scarce. Experimental methodologies which involve the measurement of the quantities included in Eqs. (6) and (8) will probably be the main source of gas-phase data.

It is also very important to have a larger database on the enthalpies of formation of the parent phenols, in order to examine substituent effects on the thermochemistry of these molecules. Combustion calorimetry—a nearly lost art—seems the right methodology to afford that information.

Finally, the "group additivity method" appears to be the best choice for predicting new data and, whenever the appropriate information is not available, the "generalized Hammett correlation" is a valid alternative.

11. Acknowledgments

This work was supported by the PRAXIS XXI Program, (Grant No. PRAXIS/2/2.1/QUI/51/94), Portugal. The authors thank Professor Mats Tilset (University of Oslo, Norway), Professor Vernon Parker (Utah State University, Utah), Dr. Wing Tsang (National Institute of Standards and Technology, Gaithersburg, MD), Edward P. Hunter (National Institute of Standards and Technology), Dr. Robert Huie (National Institute of Standards and Technology), Professor Russell Drago (University of Florida, FL), Dr. Danial Wayner (National Research Council, Canada), and Professor Benedito da Costa Cabral (Universidade de Lisboa, Portugal) for discussions or information on several issues covered by this paper.

12. Appendix

Auxiliary standard enthalpies of formation. Data in kJ mol^{-1}.[a]

Molecule	$\Delta_f H_m^\circ$ (cr/l)	$\Delta_f H_m^\circ$ (g)	Refs.
PhOH, cr	−165.1±0.7	−96.4±0.9	2
PhOMe, l	−114.8±0.8	−67.9±0.8	2
PhOEt, l	−152.6±0.6	−101.6±0.6	2
$PhOC_3H_5$		(6.9)	12
PhOBu		(−142.9)[b]	2, 12
$PhNO_2$		67.5±0.5	2
trans-N_2Ph_2, cr	308.6±1.9		2
$N_2H_2Ph_2$, cr	221.3±1.3		2
t-BuOH		−312.5±0.8	2
t-BuOOBu-*t*		−341.5±2.2	66
NO		91.265±0.43	109
H$^\bullet$		217.998±0.006	110
Me$^\bullet$		147±1	4
Et$^\bullet$		119±2	4
$C_3H_5^\bullet$		171±3	4
Bu$^\bullet$		(78±4)[c]	4

[a]Values in parentheses are estimated.
[b]Estimated from the experimental value for PhOEt and two [C–(H)$_3$(C)$_2$] group terms (see Ref. 12).
[c]Estimated by using 422 kJ mol^{-1} for the bond dissociation enthalpy of a primary C–H bond (see Ref. 4).

Additional auxiliary data:

$$\Delta_{transf}G(H^+,S\rightarrow aq) = 18.8 \text{ kJ mol}^{-1} \text{ (DMSO)};$$

$$-46.4 \text{ kJ mol}^{-1} \text{ (acetonitrile)},^{29}$$

$$T[S^\circ(PhO^\bullet,g) - S^\circ(PhOH,g)]$$

$$= -1.78 \text{ kJ mol}^{-1} \text{ (298.15 K)},^{48(a)}$$

$$\Delta_{sln}G(PhO^\bullet,g) - \Delta_{sln}G(PhOH,g)$$

$$= 12.6 \text{ kJ mol}^{-1} \text{ (water)},^{48(a)}$$

$$TS^\circ(H_2,g) = 38.93 \text{ kJ mol}^{-1} \text{ (298.15 K)},^{110}$$

$$TS^\circ(H^\bullet,g) = 34.17 \text{ kJ mol}^{-1} \text{ (298.15 K)},^{110}$$

$$\Delta_f G^\circ_m(H^\bullet,g) - 203.29 \text{ kJ mol}^{-1} \text{ (298.15 K)}.^{110}$$

13. References

[1] See, for example: (a) B. Halliwell and J. M. C. Gutteridge, *Free Radicals in Biology and Medicine*, 2nd ed. (Clarendon, Oxford, 1989). (b) *Handbook of Antioxidants*, edited by E. Cadenas and L. Packer (Marcel Dekker, New York, 1996). (c) *Lipid Oxidation in Food*, edited by A. J. St. Angelo, Am. Chem. Soc. Symp. Ser. No. 500, Washington, DC, 1992. (d) *Phenolic Compounds in Food and Their Effects on Health*; Vol. 1, edited by C.-T. Ho, C. Y. Lee, and M.-T. Huang, Am. Chem. Soc. Symp. Ser. No. 506, Washington, DC, 1992. (e) *Phenolic Compounds in Food and Their Effects on Health*, Vol. 2, edited by M.-T. Huang, C.-T. Ho, and C. Y. Lee, Am. Chem. Soc. Symp. Ser. No. 507, Washington, DC, 1992. (f) G. Scott, Chem. Br. **31**, 879 (1995), (g) Biochemist Feb./Mar. (1995).

[2] J. B. Pedley, *Thermodynamic Data and Structures of Organic Compounds*, Thermodynamics Research Center Data Series (Thermodynamics Research Center, College Station, 1994) Vol. I.

[3] *NIST Chemistry WebBook*, edited by W. G. Mallard (http://webbook.nist.gov/chemistry); NIST Standard Reference Database 69—February 1997 Release. (a) E. P. Hunter and S. G. Lias; (b) S. G. Lias and J. F. Liebman.

[4] W. Tsang, in *Energetics of Organic Radicals*, edited by J. A. Martinho Simões, A. Greenberg, and J. F. Liebman, *SEARCH Series*, Vol. 4 (Blackie, London, 1996), Chap. 2.

[5] S. W. Benson, J. Am. Chem. Soc. **87**, 972 (1965).

[6] D. H. Fine and J. B. Westmore, J. Chem. Soc., Chem. Commun., p. 273 (1969).

[7] A. S. Carson, D. H. Fine, P. Gray, and P. G. Laye, J. Chem. Soc. B, p. 1611 (1971).

[8] S. Paul and M. H. Back, Can. J. Chem. **53**, 3330 (1975).

[9] J. C. Mackie, K. R. Doolan, and P. F. Nelson, J. Phys. Chem. **93**, 664 (1989).

[10] M. H. Back, J. Phys. Chem. **93**, 6880 (1989).

[11] A. J. Colussi, F. Zabel, and S. W. Benson, Int. J. Chem. Kinet. **9**, 161 (1977).

[12] E. S. Domalski, E. D. Hearing, and V. J. Hearing, Jr., *NIST Estimation of the Chemical Thermodynamic Properties for Organic Compounds at 298.15 K* (Version 5.2) (NIST Standard Reference Database 18, National Institute of Standards and Technology: Gaithersburg, MD, 1994).

[13] S. E. Stein, *NIST Structures and Properties* (Version 2) (NIST Standard Reference Database 25; National Institute of Standards and Technology, Gaithersburg, MD, 1994).

[14] C.-Y. Lin and M. C. Lin, J. Phys. Chem. **90**, 425 (1986).

[15] M. M. Suryan, S. A. Kafafi, and S. E. Stein, J. Am. Chem. Soc. **111**, 1423 (1989).

[16] J. A. Walker and W. Tsang, J. Phys. Chem. **94**, 3324 (1990).

[17] I. W. C. E. Arends, R. Louw, and P. Mulder, J. Phys. Chem. **97**, 7914 (1993).

[18] D. J. DeFrees, R. T. McIver, Jr., and W. J. Hehre, J. Am. Chem. Soc. **102**, 3334 (1980).

[19] (a) S. H. Hoke II, S. S. Yang, R. G. Cooks, D. A. Hrovat, and W. T. Borden, J. Am. Chem. Soc. **116**, 4888 (1994); (b) R. G. Cooks, J. S. Patrick, T. Kotiaho, and S. A. McLuckey, Mass Spectrom. Rev. **13**, 287 (1994).

[20] S. G. Lias, J. F. Liebman, and R. D. Levin, J. Phys. Chem. Ref. Data **13**, 695 (1984).

[21] J. B. Cumming and P. Kebarle, Can. J. Chem. **56**, 1 (1978).

[22] J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., J. Am. Chem. Soc. **101**, 6047 (1979).

[23] M. Fujio, R. T. McIver, Jr., and R. W. Taft, J. Am. Chem. Soc. **103**, 4017 (1981).

[24] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *NIST Negative Ion Energetics Database* (Version 3.00) (NIST Standard Reference Database 19B, Gaithersburg, MD, 1993).

[25] R. F. Gunion, M. K. Gilles, M. L. Polak, and W. C. Lineberger, Int. J. Mass Spectrom. Ion Processes **117**, 601 (1992).

[26] The heat capacity change of reactions (10) and (12) could not be estimated by additivity methods, due to the absence of some group terms. It was assumed that the $\Delta_r C^\circ_p$ of those reactions are comparable to the values for PhOH(g)→Ph$^\bullet$(g)+$^\bullet$OH(g), $\sim$6.5 J mol^{-1} K^{-1}, and PhMe(g)→Ph$^\bullet$(g)+Me$^\bullet$(g), $\sim$12.5 J mol^{-1} K^{-1}, respectively. See Ref. 13 and M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed.; J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985). These are the $\Delta_r C^\circ_p$ values at 300 K and lead to upward temperature corrections of 1.9 and 3.7 kJ mol^{-1} in the enthalpies of reactions (10) and (12), respectively.

[27] J. M. Kanabus-Kaminska, B. C. Gilbert, and D. Griller, J. Am. Chem. Soc. **111**, 3311 (1989).

[28] D. D. M. Wayner, E. Lusztyk, D. Pagé, K. U. Ingold, P. Mulder, L. J. J. Laarhoven, and H. S. Aldrich, J. Am. Chem. Soc. **117**, 8737 (1995).

[29] V. D. Parker, J. Am. Chem. Soc. **114**, 7458 (1992); **115**, 1201 (1993).

[30] L. R. Mahoney and M. A. DaRooge, J. Am. Chem. Soc. **97**, 4722 (1975).

[31] It is considered that the reaction enthalpy is the same at 298 K. The assumption of a negligible entropy change was experimentally observed in the case of reaction (15), for which $\Delta_r S = 0 \pm 5.0$ J mol^{-1} K^{-1}.

[32] L. R. Mahoney and M. A. DaRooge, J. Am. Chem. Soc. **92**, 4063 (1970).

[33] L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, J. Am. Chem. Soc. **91**, 3883 (1969).

[34] Mahoney and DaRooge derived $\Delta_f H^\circ_m(AH, sln) - \Delta_f H^\circ_m(A^\bullet, sln) = -121.0$ kJ mol^{-1}. The discrepancy is due to a different choice of the enthalpy of formation of *trans*-azobenzene.

[35] See, for example, the references indicated in Ref. 28.

[36] R. S. Drago, A. P. Dadmun, and G. C. Vogel, Inorg. Chem. **32**, 2473 (1993).

[37] G. C. Vogel and R. S. Drago, J. Chem. Ed. **73**, 701 (1996).

[38] The interaction of PhOH with benzene is calculated as -8.7 kJ mol^{-1}. The proton affinity of chlorobenzene is only 3 kJ mol^{-1} higher than benzene.

[39] D. D. M. Wayner and V. D. Parker, Acc. Chem. Res. **26**, 287 (1993).

[40] F. G. Bordwell, J.-P. Cheng, and J. A. Harrelson, Jr., J. Am. Chem. Soc. **110**, 1229 (1988).

[41] F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, and X. Zhang, J. Am. Chem. Soc. **113**, 9790 (1991).

[42] F. G. Bordwell and X. Zhang, Acc. Chem. Res. **26**, 510 (1993).

[43] F. G. Bordwell and J.-P. Cheng, J. Am. Chem. Soc. **113**, 1736 (1991).

[44] F. G. Bordwell and X. Zhang, J. Phys. Org. Chem. **8**, 529 (1995).

[45] F. G. Bordwell and W.-Z. Liu, J. Am. Chem. Soc. **118**, 10819 (1996).

[46] The enthalpy of solvation of the hydrogen atom (5 ± 1 kJ mol^{-1}) has not been included in the correction, since it is considered to be included in the empirical constant of Eq. (21).

[47] E. M. Arnett and R. A. Flowers II, Chem. Soc. Rev. **22**, 9 (1993).

[48] (a) J. Lind, X. Shen, T. E. Eriksen, and G. Merényi, J. Am. Chem. Soc. **112**, 479 (1990); (b) See Ref. 39.

[49] The auxiliary data in the Appendix and Eq. (20) can be used to calculate the constant of Eq. (21) as 223.1 kJ mol^{-1}. This value is only valid for aqueous solution and for the phenol system. Parker (Ref. 29) has published equations of the same type, derived for different solvents. There are, however, some typos in his paper, not revised in the later "Additions and Corrections." Most notably, in his equation (d), which is equivalent to Eq. (20), the term $TS^\circ(H^\bullet,g)$ should be replaced by $TS^\circ(H^\bullet,g)$ and a minus sign should appear before the Gibbs energy of transfer.

[50](a) E. M Arnett, K. Amarnath, N. G. Harvey, and S. Venimadhavan, J. Am. Chem. Soc. **112**, 7346 (1990); (b) Later work by another group. [C. P. Andrieux, P. Hapiot, J. Pinson, and J.-M. Savéant, *ibid.* **115**, 7783 (1993)] has shown that the use of second-harmonic ac voltammetry does not avoid the irreversibility problem. This is only accomplished by experiments made in faster time scales.

[51]See, for example, K. S. Peters, Angew. Chem. Int. Ed. Engl. **33**, 294 (1994); S. E. Braslavsky and G. E. Heibel, Chem. Rev. **92**, 1381 (1992); D. Griller and D. D. M. Wayner, Pure Appl. Chem. **61**, 717 (1989).

[52]P. Mulder, O. W. Saastad, and D. Griller, J. Am. Chem. Soc. **110**, 4090 (1988).

[53]See, for example, K. B. Clark, D. D. M. Wayner, S. H. Demirdji, and T. H. Koch, J. Am. Chem. Soc. **115**, 2447 (1993).

[54]W. Tsang, J. Phys. Chem. **90**, 1152 (1986).

[55]Tsang, in Ref. 54, calculated D(C–H)=318 kJ mol^{-1}, based on older auxiliary data. This was the value used by Wayner *et al.* (Ref. 28).

[56]M. Lucarini, P. Pedrielli, G. F. Pedulli, S. Cabiddu, and C. Fattuoni, J. Org. Chem. **61**, 9259 (1996).

[57]C. D. Cook, C. B. Depatie, and E. S. English, J. Org. Chem. **24**, 1356 (1959).

[58]L. R. Mahoney and M. A. DaRooge, J. Am. Chem. Soc. **92**, 890 (1970).

[59]X.-M. Zhang and F. G. Bordwell, J. Am. Chem. Soc. **116**, 4251 (1994).

[60]Y. Zhao and F. G. Bordwell, J. Am. Chem. Soc. **118**, 6623 (1996).

[61]M. J. Bausch, R. Gostowski, C. Guadalupe-Fasano, D. Selmarten, A. Vaughn, and L.-H. Wang, J. Org. Chem. **56**, 7191 (1991).

[62]L. E. Friedrich, J. Org. Chem. **48**, 3851 (1983).

[63]The bond dissociation enthalpies derived by Friedrich are significantly higher than those obtained here, due to the use of different auxiliary data and also of some assumptions. For example, the values estimated by Friedrich, which are solution values, assume that the entropy changes of reactions (33) and (34) are equal to $S°(H^•,aq)$.

[64]V. D. Parker, J.-P. Cheng, and K. L. Handoo, Acta Chem. Scand. **47**, 1144 (1993).

[65]The enthalpy of solvation of gaseous H$^•$ was taken as 5 kJ mol^{-1} (see Sec. 3). The entropy difference between the phenoxy radical and its parent compound was identified with the difference for PhO$^•$ and PhOH (Appendix). The difference $\Delta_{sln}S(R^•,g)-\Delta_{sln}S(RH,g)$ was neglected but it will be positive (hence the lower limit assigned to the value). Finally, the gas phase D(O–H) was calculated from D_{sln}(O–H), as described in Sec. 3 (see also Table 3), assuming that ΔH(ECW) for **12** and PhOH are identical.

[66]H. P. Diogo, M. E. Minas da Piedade, J. A. Martinho Simões, and Y. Nagano, J. Chem. Thermodyn. **27**, 597 (1995).

[67]D. D. M. Wayner, E. Lusztyk, K. U. Ingold, and P. Mulder, J. Org. Chem. **61**, 6430 (1996).

[68]The exceptions, 3-$CF_3C_6H_4OH$ and 4-NCC_6H_4OH, are stronger acids than phenol (see Ref. 67) and therefore the gas phase O–H bond dissociation enthalpies will be at least 13.7 kJ mol^{-1} lower than the solution values in Table 4.

[69]M. E. J. Coronel and A. J. Colussi, Int. J. Chem. Kinet. **20**, 749 (1988).

[70]R. A. Jackson and K. M. Hosseini, J. Chem. Soc., Chem. Commun. p. 967 (1992).

[71]M. Lucarini, G. F. Pedulli, and M. Cipollone, J. Org. Chem. **59**, 5063 (1994).

[72]M. E. J. Coronel and A. J. Colussi, J. Chem. Soc. Perkin Trans. 2 p. 785 (1994).

[73]The rather small $\Delta_rS(42)$ values obtained for X=OMe and *t*-Bu indicate that the error introduced by this assumption is smaller than ~2 kJ mol^{-1}.

[74]A. L. Castelhano and D. Griller, J. Am. Chem. Soc. **104**, 3655 (1982).

[75]C. Rousseau-Richard, C. Richard, and R. Martin, J. Chim. Phys. **86**, 2057 (1989).

[76]V. A. Roginskii and G. A. Krasheninnikova, Kinet. Catal. **28**, 271 (1987).

[77]Most of the available electron affinity values of phenoxy radicals in Ref. 24 were calculated from Eq. (8) by using $\Delta_{acid}H$ data and O–H bond dissociation energies estimated from solution studies.

[78]M. M. Suryan, S. A. Kafafi, and S. E. Stein, J. Am. Chem. Soc. **111**, 4594 (1989).

[79]Y.-D. Wu and D. K. W. Lai, J. Org. Chem. **61**, 7904 (1996).

[80]Calculated data for O–H bond dissociation enthalpies which were not subject to experimental determination were not included in Table 4.

[81]J. S. Wright, D. J. Carpenter, D. J. McKay, and K. U. Ingold, J. Am. Chem. Soc. **119**, 4245 (1997).

[82]T. Brinck, M. Haeberlein, and M. Jonsson, J. Am. Chem. Soc. **119**, 4239 (1997).

[83]B. J. Costa Cabral (unpublished results).

[84]M. Jonsson, J. Lind, T. E. Eriksen, and G. Merényi, J. Chem. Soc., Perkin Trans. 2, p. 1567 (1993).

[85]G. W. Burton, T. Doba, E. J. Gabe, L. Hughes, F. L. Lee, L. Prasad, and K. U. Ingold, J. Am. Chem. Soc. **107**, 7053 (1985).

[86]F. G. Bordwell, X.-M. Zhang, A. V. Satish, and J.-P. Cheng, J. Am. Chem. Soc. **116**, 6605 (1994).

[87]V. A. Roginskii, Vysokomol. Soyed. **A24**, 1808 (1982).

[88]*Parent contributions* have also been named *ground state effects* and *polar contributions*.

[89]C. D. Johnson, *The Hammett Equation* (Cambridge University Press, Cambridge, 1980).

[90]J. March, *Advanced Organic Chemistry*, 4th ed. (Wiley, New York, 1992).

[91]C. Hansch, A. Leo, and R. W. Taft, Chem. Rev. **91**, 165 (1991).

[92]Different σ^+ data sets were used in Refs. 52, 78, and 84.

[93]See, for example, J. A. Martinho Simões and J. L. Beauchamp, Chem. Rev. **90**, 629 (1990), and references cited therein.

[94]In the case of large resonance effects, these may also be felt at the *meta* position, although they are expected to be small compared to the inductive effects.

[95]K. B. Clark, and D. D. M. Wayner, J. Am. Chem. Soc. **113**, 9363 (1991).

[96]L. J. J. Laarhoven, J. G. P. Born, I. W. C. E. Arends, and P. Mulder, J. Chem. Soc. Perkin Trans. 2, 2307 (1997).

[97]S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976).

[98]J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970).

[99]The difference in ΔD(O–H), observed in Table 4, between the "away" and "toward" conformers of 3-methylphenol is not zero, as it should be expected. This must be due to the limitations of the calculation method.

[100]ΔD(O–H) for 4-$CHOC_6H_4OH$, estimated with Eqs. (49) and (51), is, respectively, 20 kJ mol^{-1} ($\sigma_p^-=0.73$) and 9 kJ mol^{-1} ($\sigma_p=0.42$). The latter value was preferred. The Hammett parameters were quoted from Ref. 91.

[101]The dihedral angles C(sp^2)–C(sp^2)–O–C reported by Ingold and coworkers are ~17° for the chromanol **19** (a model for α-tocopherol, where the phytyl chain is replaced by CH_3), ~6° for the dihydrobenzofuranol **17**, and 89° for 4-methoxytetramethylphenol.

[102]ΔD(O–H) for 4-$MeSC_6H_4OH$ was estimated with Eq. (52) with $\sigma_p^+=-0.60$.

[103]After the discussion above, the point for 2-NO_2 was excluded from the correlation.

[104]As stated in Ref. 81, the parameter a should not even be constant for all substituents.

[105]With $a=1$ the correlation is also good ($r=0.974$).

[106]E. T. Denisov, Polym. Degrad. Stab. **49**, 71 (1995).

[107]E. T. Denisov, Zh. Fiz. Khim. **69**, 623 (1995).

[108]E. Denisov, *Handbook of Antioxidants* (CRC, Boca Raton, FL, 1995).

[109]*Thermodynamic Properties of Individual Substances*, 3rd ed., edited by V. P. Glushko (Nauka, Moscow, 1978–1982), Vols. 1–4.

[110]J. D. Cox, D. D. Wagman, and V. A. Medvedev, *Codata Key Values for Thermodynamics* (Hemisphere, New York, 1989).

[111]G. T. Fogg and W. Gerrard, *Solubility of Gases in Liquids* (Wiley, Chichester, 1991).

[112]E. Wilhelm and R. Battino, Chem. Rev. **73**, 1 (1973).

[113]E. Wilhelm, R. Battino, and R. J. Wilcock, Chem. Rev. **77**, 219 (1977).