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Solvation effects of H_2O and DMSO on the O—H bond dissociation energies of substituted phenols

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ABSTRACT: Solvation effects on the O—H homolytic bond dissociation energies (BDEs) of substituted phenols were studied. It was demonstrated that the BDEs measured in solution in general do not equal the BDEs in the gas phase. Detailed theoretical analyses indicated that a long-range solvation effect (i.e. the interaction between the solvent and the overall dipole moment of the solute) and a short-range solvation effect (i.e. the hydrogen bonding between the solute and solvent) were both important for the O—H BDEs in water and in DMSO. Neither one of these two factors by itself could fully explain the experimentally observed solvation effect. However, a combination of these two factors, estimated through a semi-continuum solvation model, was shown to be reasonably successful in explaining the experimental results. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: bond dissociation energy; homolysis; radical; solvation energy; solvent effect; PCM; hydrogen bond

INTRODUCTION

The O—H bond dissociation energies (BDEs) of phenols are important descriptors to characterize the radical-scavenging activity of phenolic antioxidants.[1] Therefore, a number of experimental studies have been conducted in an attempt to measure the O—H BDEs of various substituted phenols.[2] A few theoretical studies have also been performed in order to elucidate the quantitative structure–activity relationship behind these BDEs.[3] One key finding from these studies is that substituent effects on the O—H BDEs of phenols can be described using the conventional Hammett equation:

$$\mathrm{BDE(X\text{-}C_6H_4\text{-}OH)} - \mathrm{BDE(C_6H_5\text{-}OH)} = \rho^+\sigma^+ \quad (1)$$

Both the experimental and theoretical BDEs can be used to calculate the ρ^+ value as shown in Eqn (1) (Table 1). Using Bordwell *et al.*'s BDEs, the ρ^+ value for the O—H BDEs of phenols was calculated to be $8.1\,\mathrm{kcal\,mol^{-1}}$ ($1\,\mathrm{kcal} = 4.184\,\mathrm{kJ}$).[2e] This value is in agreement with the ρ^+ value ($8.3\,\mathrm{kcal\,mol^{-1}}$) calculated using the experimental O—H BDEs reported by Lind *et al.*[2d] However, using the B3LYP/6–31G* method, Wu and Lai obtained a ρ^+ value of $5.9\,\mathrm{kcal\,mol^{-1}}$.[3a] Using B3LYP/6–31G**, Brinck *et al.* obtained a ρ^+ value of $5.7\,\mathrm{kcal\,mol^{-1}}$.[3b] Our ρ^+ value, calculated using the UB3LYP/6–311++G(2df,p) method is $5.6\,\mathrm{kcal\,mol^{-1}}$.

The noteworthy disagreement between the experimental and theoretical ρ^+ values might indicate that density functional theory cannot precisely predict the substituent effects. However, it is also possible that the experimental results are problematic. At this point, it should be noted that BDE is normally defined as the gas-phase enthalpy change of the reaction $\mathrm{X—Y} \rightarrow \mathrm{X^\bullet} + \mathrm{Y^\bullet}$. However, Bordwell *et al.*'s experimental O—H BDEs were estimated from the one-electron reduction potential of the phenoxyl radical measured by cyclic voltammetry and the pK_a of the phenol in DMSO using Hess's law. Lind *et al.*'s experimental O—H BDEs were estimated from the one-electron reduction potential of the phenoxyl radical measured by pulse radiolysis and the pK_a of the phenol in aqueous solution, again using Hess's law.

An assumption in both Bordwell *et al.*'s and Lind *et al.*'s studies is that the difference in the solvation free energy between the phenol and phenoxyl radical is independent of substitution. However, it was shown by Pedrielli and Pedulli[4] that phenolic O—H BDEs in benzene and in *tert*-butyl alcohol are different by $1–2\,\mathrm{kcal\,mol^{-1}}$. After a detailed examination of their results, one can also see that the difference in BDEs is not independent of substitution. On the basis of Pedrielli and Pedulli's observations, it is evident that the ρ^+ value estimated using Bordwell *et al.*'s or Lind *et al.*'s BDEs contains substantial contributions from solvation effects.

The problem of solvation effects on BDEs has also been mentioned in a recent review by Laarhoven *et al.*[5] Certainly the involvement of solvation effects does not

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Table 1. BDE(X—C_6H_4—OH)−BDE(C_6H_5—OH) values from experimental measurements and from theoretical calculations (kcal mol^{-1})

Substituent	σ_p^+[a]	Exp. (DMSO)[b]	Exp. (H_2O)[c]	B3LYP/6–31 G*[d]	B3LYP/ 6–31G**[e]	UB3LYP/ 6–311++G(2df,p)[f]
p-NH_2	−1.30	−12.6	−12.7	−9.1	−8.6	−8.7
p-OH	−0.92	−8.3	−8.0	−6.3	−5.4	−5.2
p-OCH_3	−0.78	−5.3	−5.6	−6.0	−5.5	−5.7
p-Me	−0.31	−1.1	−2.1	−1.9	−1.8	−2.2
p-Cl	0.11	0.4	−0.6	−1.0	−0.7	−1.3
H	0.00	0.0	0.0	0.0	0.0	0.0
p-CF_3	0.61	5.5	—	2.4	2.6	2.7
p-CN	0.66	4.4	4.7	1.9	2.3	2.1
p-NO_2	0.79	4.5	6.0	4.1	4.4	4.2
ρ^{+g}	—	8.1	8.3	5.9	5.7	5.6
r^h	—	0.980	0.989	0.988	0.990	0.986

[a] Taken from Ref. 20.
[b] Taken from Ref. 2e. It is noteworthy that Bordwell *et al.* reported a 'revised' reaction constant (7.14 kcal mol^{-1}) in 1994.[2f] However, this 'revised' reaction constant was calculated from a plot containing a few dubious data such as the O—H BDE of 4-Me_2N—C_6H_4—OH.
[c] Taken from Ref. 2d.
[d] Taken from Ref. 3a.
[e] Taken from Ref. 3e.
[f] This study.
[g] ρ^+ values are calculated as the slope of Eqn (1).
[h] Correlation coefficient.

mean that Bordwell *et al.*'s or Lind *et al.*'s measurements are flawed. As long as one keeps in mind that Bordwell *et al.*'s or Lind *et al.*'s BDEs are solution-phase BDEs whose values may be different from those in the gas phase, there will be no controversy between the theory and experiment. It is worth noting that for practical purposes, most chemical processes of interest to chemists and biochemists usually occur in solution and therefore direct measurement of BDEs in solution is sometimes more important. Nevertheless, when one talks about the intrinsic bond strength, one has to use the gas-phase BDE.

The purpose of this work was to acquire a clear understanding about how the solvation process affects the O—H BDEs using theoretical approaches. There are two major questions to answer in the study: (1) what factors are responsible for the change of the ρ^+ value from the gas phase to the solution? and (2) can we quantitatively calculate the solvation effects on the ρ^+ value? The results from this study may be valuable for those who try to use solution-phase thermodynamics to derive the intrinsic bond strengths (i.e. BDE of an isolated molecule in the gas phase). The same results may also be valuable for those who try to use the intrinsic bond strength to interpret the equilibrium or kinetics of a radical reaction in solution.

EXPERIMENTAL

All the calculations were carried out using the Gaussian 98 suite of programs.[6] The geometry of each species was optimized using the UB3LYP/6–31G(d) method. For those molecules or complexes which have more than one possible conformation, the conformation with the lowest electronic energy was singled out and used for the following calculations. Each final optimized geometry was confirmed by the UB3LYP/6–31G(d) frequency calculation to be a real minimum on the potential energy surface without any imaginary frequency.

Harmonic vibrational frequencies were calculated using the UB3LYP/6–31G(d) method for the optimized geometries. Zero-point vibrational energy corrections were obtained using unscaled frequencies. The enthalpy of each species in the gas phase at 298 K was calculated using the UB3LYP/6–311++G(2df,p) method using the following equation within the rigid rotor and harmonic oscillator approximation:

$$H_{298} = E + ZPE + \Delta H_{298-0} \quad (2)$$

The gas-phase BDE of each phenol molecule (X—C_6H_4—OH) was calculated as the enthalpy change in the gas phase at 298 K of the following reaction:

$$X\text{-}C_6H_4\text{-}OH \rightarrow X\text{-}C_6H_4\text{-}O^\bullet + H^\bullet \quad (3)$$

Because the UB3LYP method usually underestimates the BDEs (for an authoritive study on the performance of the B3LYP method, see Ref. 7) (higher level methods such as G3 or CBS are too demanding for the phenols), in the present study we only report the relative BDEs [i.e. BDE(X—C_6H_4—OH)−BDE(C_6H_5—OH)]. According to recent studies,[7,8] these relative BDEs should be reasonably reliable owing to the error cancellation from C_6H_5—OH to X—C_6H_4—OH.

Two approaches were used to model the solvation effects. In the first approach, an explicit complex between the substrate and a solvent molecule was constructed. For

Table 2. BDE(X—C_6H_4—OH)−BDE(C_6H_5—OH) values calculated using the UB3LYP/6–311++g(2df,p)–PCM method in the gas phase, H_2O, and DMSO (kcal mol^{-1})

Substituent	σ_p^+	Vacuum	H_2O	DMSO	$\mu^c_{X-C_6H_4-OH}$	$\mu^d_{X-C_6H_4-O^\bullet}$	$\Delta\mu^{2e}$
p-NH_2	−1.30	−8.7	−11.0	−9.6	2.048	6.841	42.605
p-OH	−0.92	−5.2	−6.5	−5.7	0.001	4.870	23.717
p-OCH_3	−0.78	−5.7	−6.9	−5.6	0.575	5.722	32.411
p-Me	−0.31	−2.2	−3.6	−2.3	1.360	4.798	21.171
p-Cl	0.11	−1.3	−1.2	−0.6	2.306	2.808	2.567
H	0.00	0.0	0.0	0.0	1.336	4.023	14.400
p-CF_3	0.61	2.7	2.8	3.6	3.442	1.160	−10.502
p-CN	0.66	2.1	3.5	4.1	5.297	0.357	−27.931
p-NO_2	0.79	4.2	4.5	5.7	5.364	0.899	−27.964
ρ^{+a}	—	5.6	7.0	6.8	—	—	—
r^b	—	0.986	0.991	0.994	—	—	—

[a] ρ^+ values are calculated as the slope of Eqn (1).
[b] Correlation coefficient.
[c] Dipole moment of X—C_6H_4—OH (D).
[d] Dipole moment of X—C_6H_4—$O^\bullet$ radical (D).
[e] $\Delta\mu^2 = \mu^2_{X-C_6H_4-O^\bullet} - \mu^2_{X-C_6H_4-OH}$.

a phenol substrate and water or DMSO solvent, this complex is likely to be stabilized by a hydrogen bond. The hydrogen bonding energy was calculated as the enthalpy change of the following reaction in the gas phase at 298 K:

$$\text{substrate} + \text{solvent} \rightarrow \text{complex} \qquad (4)$$

The basis set superposition error (BSSE) was considered for the hydrogen bonding energy using the full counterpoise procedure.[9]

In the second approach to model the solvation effects, we used a continuum description of the solvent based on the SCRF method at the UB3LYP/6–311++G(2df,p) level. The gas-phase geometry was used. The polarized continuum model (PCM) developed by Tomasi and coworkers[10] was employed. With this method, the mean error with respect to the experimental absolute solvation energies in water was reported as about 0.2 and 1 kcal mol^{-1} for neutral molecules and ions, respectively. Although radicals were not considered in Tomasi and coworkers' parameterization work, a recent study indicated that the PCM method may work well for open-shell species.[11]

It is worth noting that Tomasi and co-workers did not parameterize their PCM model for DMSO. Fortunately, Pliego and Riveros recently reported a parameterization of the PCM model for calculating solvation free energies of anions in DMSO.[12] Their scale factor for the atomic radii is $f = 1.35$. Our own examination on the basis of Bondi radii[13] also provided a scale factor of 1.35 for both anions and neutral molecules (Y. Fu, L. Liu, Q.-X. Guo, unpublished results). It should be mentioned that this scale factor does not work well for cations in DMSO.[12]

The PCM method provides the solvation free energy. (The gas-phase enthalpies correspond to a standard state of 1 atm and 298 K. The solvation free energy of PCM corresponds to a standard state of 1 mol l^{-1} and 298 K. Although the states are different, for relative values the state correction term from 1 atm to 1 mol l^{-1} is cancelled.) However, one can assume that the entropy contribution for X—C_6H_4—OH homolysis equals that for C_6H_5—OH homolysis.[4] On the basis of this assumption, [BDE(X—C_6H_4—OH)−BDE(C_6H_5—OH)]$_{solution\ phase}$ should equal the sum of [BDE(X—C_6H_4—OH)−BDE (C_6H_5—OH)]$_{gas\ phase}$ and change of solvation free energies. Therefore, in the following only the enthalpy changes will be considered for both the gas and solution phases.

RESULTS AND DISCUSSION

Fully implicit method

In Table 2 are shown the BDE(X—C_6H_4—OH)−BDE(C_6H_5—OH) values in the gas phase, in H_2O and in DMSO calculated using the UB3LYP/6–311++g(2df,p)-PCM method.

According to Table 2, an electron-donating substituent usually reduces the phenolic O—H BDE more significantly in the solution than in the gas phase. For example, *p*-NH_2 lowers the O—H BDE by 8.7 kcal mol^{-1} in the gas phase. In comparison, *p*-NH_2 lowers the O—H BDE by 11.0 kcal mol^{-1} in H_2O and by 9.6 kcal mol^{-1} in DMSO. On the other hand, an electron-withdrawing substituent increases the phenolic O—H BDE more significantly in the solution that in the gas phase. For instance, *p*-CN increases the phenolic O—H BDE by 2.1 kcal mol^{-1} in the gas phase. In comparison, *p*-CN increases the phenolic O—H BDE by 3.5 kcal mol^{-1} in H_2O and by 4.1 kcal mol^{-1} in DMSO.

The larger BDE reduction effects seen for the donor groups and larger BDE increase effects seen for the acceptor groups can be understood using the Bell

model.[14] According to this model, the solvation free energy of a ball which contains a point dipole μ at the center follows Eqn (5), where ε is the dielectric constant of the solvent, μ is the dipole moment and R is the radius of the ball:

$$\Delta G = -\frac{\varepsilon - 1}{2\varepsilon + 1}\frac{\mu^2}{R^3} \quad (5)$$

According to the Bell model, one can expect a larger solvation free energy with a larger μ^2 when other parameters such as ε and R are similar. From Table 2, it is evident that when X is a donor substituent, μ^2 increases from X—C_6H_4—OH to X—C_6H_4—O$^\bullet$. This is not a surprising observation because O$^\bullet$ is strongly electron withdrawing whereas OH is modestly electron donating. Therefore, X—C_6H_4—O$^\bullet$ should have a larger solvation free energy than X—C_6H_4—OH when X is the donor.

Notably, from C_6H_5—OH to C_6H_5—O$^\bullet$, μ^2 also increases by 14.400 D^2. Therefore, only those donor substituents which can cause a larger increase in μ^2 than H can bring about a larger reduction of O—H BDE in the solution than in the gas phase. According to Table 2, NH_2, OH, OCH_3 and CH_3 increase μ^2 by 42.605, 23.717, 32.411, and 21.171 D^2 from X—C_6H_4—OH to X—C_6H_4—O$^\bullet$. These values are larger than 14.400, and the corresponding groups indeed reduce the O—H BDE more significantly in the solution than in the gas phase. An exceptional donor group is Cl, which increases the dipole moment only by 2.567 D^2 from Cl—C_6H_4—OH to Cl—C_6H_4—O$^\bullet$, a value smaller than 14.400. Therefore, Cl should cause a smaller reduction of O—H BDE in the solution than in the gas phase. This prediction agrees with the calculated results.

Unlike the donor groups, an acceptor group decreases μ^2 from X—C_6H_4—OH to X—C_6H_4—O$^\bullet$ due to the electron-withdrawing nature of O$^\bullet$. The consequence of this reduction of μ^2 is that the solvation free energy of X—C_6H_4—O$^\bullet$ is smaller than that of X—C_6H_4—OH. Compared with the unsubstituted case, it is clear that an acceptor group should cause a larger increase of the O—H BDE in the solution than in the gas phase.

The fact that a donor causes a larger BDE reduction and an acceptor causes a larger BDE increase in solution than in the gas phase means that ρ^+ for the O—H BDEs in solution should be larger than that for the gas phase. Indeed, the calculated ρ^+ values are 7.0 kcal mol^{-1} for H_2O and 6.8 kcal mol^{-1} for DMSO. Both values are larger than the ρ^+ value for the gas phase (5.6 kcal mol^{-1}). These results substantiate the argument that the solvent should not be neglected for the BDEs measured using a solution-phase method. However, compared with Bordwell *et al.*'s (8.1 kcal mol^{-1}) and Lind *et al.*'s (8.3 kcal mol^{-1}) ρ^+ values, the theoretical ρ^+ value obtained using the PCM method is still lower by 1.1–1.3 kcal mol^{-1}.

Hydrogen bonding with solvent molecules

As an implicit solvation model, PCM cannot fully describe the first solvation shell interactions, such as hydrogen bonding between the solute and solvent molecules.[15] However, it is well established that hydrogen bonding may considerably affect a BDE value (for some recent examples, see Ref. 16). Therefore, the difference between the experimental and theoretical ρ^+ values obtained in the previous section might be due to the incomplete consideration of the solute–solvent hydrogen bonding effects.

To model the solute–solvent hydrogen bonding effect, we focused our attention on the complexes between phenol (or phenoxyl radical) and one H_2O (or DMSO) molecule. Certainly one can consider more solvent molecules and construct a larger solute–solvent hydrogen-bonded cluster. However, using this approach one might end up with a large number of complexation conformations that are local minima. The necessity to average over the many possible conformations makes this large-cluster approach unwieldy, especially under the present conditions where a number of substituted phenols and phenoxyl radicals will be studied.

The optimized structures of the phenol–H_2O, phenol–DMSO, phenoxyl radical–H_2O, and phenoxyl radical–DMSO complexes are shown in Fig. 1. As shown in Fig. 1, phenol is a hydrogen bond donor. The O—H···O distance in the phenol–H_2O complex is 1.831 Å. This value is slightly longer than the O—H···O distance (1.743 Å) in the phenol–DMSO complex. In agreement with these geometric features, the hydrogen bonding energy of phenol–H_2O (-3.8 kcal mol^{-1}) is smaller than that of phenol–DMSO (-7.1 kcal mol^{-1}).

In comparison, phenoxyl radical is a hydrogen bond acceptor in the phenoxyl radical–H_2O complex. The hydrogen bonding energy for this complex is -3.4 kcal mol^{-1}, a value not much lower than that for the phenol–H_2O complex. Interestingly, in the phenoxyl

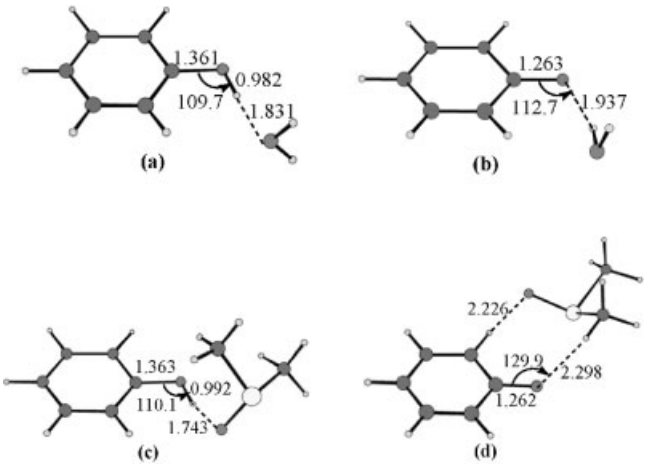

Figure 1. Structures of the hydrogen-bonded complexes between phenol or phenoxyl radical and H_2O or DMSO

Table 3. Hydrogen bonding energies in X—C_6H_4—OH···H_2O, X—C_6H_4—$O^{\bullet}$···H_2O, X—C_6H_4—OH···DMSO, and X—C_6H_4—$O^{\bullet}$···DMSO complexes calculated using the UB3LYP/6–311++g(2df,p) method in the gas phase (BSSE corrected) (kcal mol^{-1})

Substituent	σ_p^+	X—C_6H_4—OH ···H_2O	X—C_6H_4—$O^{\bullet}$ ···H_2O	X—C_6H_4—OH ···DMSO	X—C_6H_4—$O^{\bullet}$ ···DMSO
p-NH_2	−1.30	−3.1	−4.5	−6.6	−2.8
p-OH	−0.92	−3.6	−4.1	−6.9	−3.2
p-OCH_3	−0.78	−3.5	−4.0	−6.8	−2.5
p-Me	−0.31	−3.6	−3.6	−6.8	−2.7
p-Cl	0.11	−4.4	−3.3	−7.8	−2.9
H	0.00	−3.8	−3.4	−7.1	−2.7
p-CF_3	0.61	−4.8	−2.9	−8.4	−3.1
p-CN	0.66	−5.3	−3.1	−8.9	−3.4
p-NO_2	0.79	−5.5	−3.0	−9.3	−3.3
ρ^+	—	−1.1	0.7	−1.2	−0.2
r	—	0.932	0.986	0.906	0.569

radical–DMSO complex the phenoxyl radical is both a hydrogen bond donor and acceptor, as two C—H···O hydrogen bonds[17] can be identified. Because a C—H···O hydrogen bond is much weaker than an O—H···O hydrogen bond, the hydrogen bonding energy for the phenoxyl radical–DMSO complex (−2.7 kcal mol^{-1}) is much lower than that for the phenol–DMSO complex.

Because phenol is the hydrogen bond donor in X—C_6H_4—OH···H_2O, it is understandable that an electron-withdrawing substituent brings about a larger hydrogen bonding energy than an electron-donating substituent (see Table 3). This means that the ρ^+ value for the hydrogen bonding energy of X—C_6H_4—OH···H_2O is negative (−1.1 kcal mol^{-1}). In comparison, because phenoxyl radical is the hydrogen bond acceptor, the ρ^+ value for the hydrogen bonding energy of X—C_6H_4—$O^{\bullet}$···H_2O should be positive (+0.7 kcal mol^{-1}). Therefore, for the gas-phase reaction X—C_6H_4—OH···H_2O → X—C_6H_4—$O^{\bullet}$···H_2O + $H^{\bullet}$, one may predict the corresponding reaction constant as $\rho^+ = 5.6 + 0.7 - (-1.1) = 7.4$ kcal mol^{-1}. This prediction is in good agreement with the actual calculated result, 7.6 kcal mol^{-1} (see Table 4).

Because phenol is the hydrogen bond donor in X—C_6H_4—OH···DMSO, the ρ^+ value for the hydrogen bonding energy of X—C_6H_4—OH···DMSO should be negative (−1.2 kcal mol^{-1}). In comparison, because phenoxyl radical is both the hydrogen bond donor and acceptor, the ρ^+ value for the hydrogen bonding energy of X—C_6H_4—$O^{\bullet}$···DMSO should be close to zero (−0.2 kcal mol^{-1}). For the gas-phase reaction X—C_6H_4—OH···DMSO → X—C_6H_4—DMSO···H_2O + $H^{\bullet}$, , one may predict the corresponding reaction constant as $\rho^+ = 5.6 - 0.2 - (-1.2) = 6.6$ kcal mol^{-1}. This prediction is also in good agreement with the actual result of the calculation, 6.7 kcal mol^{-1} (Table 4).

It is worth noting that the X—C_6H_4—OH···H_2O and X—C_6H_4—$O^{\bullet}$···H_2O complexes may be regarded as a microsolvation model of X—C_6H_4—OH and X—C_6H_4—$O^{\bullet}$. As a result, the gas-phase reaction X—C_6H_4—OH···H_2O → X—C_6H_4—$O^{\bullet}$···H_2O + $H^{\bullet}$ tells us how the microsolvation effects change the O—H BDEs. According to Table 4, the ρ^+ value for the gas-phase BDEs of X—C_6H_4—OH···H_2O complexes is 7.6 kcal mol^{-1}. The ρ^+ value for the gas-phase BDEs of X—C_6H_4—OH···DMSO complexes is 6.7 kcal mol^{-1}.

Table 4. Relative O—H BDEs of X—C_6H_4—OH···H_2O and X—C_6H_4—OH···DMSO complexes calculated using the UB3LYP/6–311++g(2df,p)-PCM method in the gas phase and in solution (kcal mol^{-1})

		X—C_6H_4—OH···H_2O		X—C_6H_4—OH···DMSO	
Substituent	σ_p^+	Vacuum	H_2O	Vacuum	DMSO
p-NH_2	−1.30	−10.4	−12.5	−9.6	−10.1
p-OH	−0.92	−6.0	−6.5	−5.9	−5.8
p-OCH_3	−0.78	−6.4	−7.8	−5.9	−6.3
p-Me	−0.31	−3.2	−4.9	−2.4	−2.5
p-Cl	0.11	2.1	1.0	−0.9	−0.7
H	0.00	0.0	0.0	0.0	0.0
p-CF_3	0.61	4.2	4.5	3.6	3.8
p-CN	0.66	4.0	4.6	3.2	4.3
p-NO_2	0.79	6.5	6.9	5.7	7.0
ρ^+	—	7.6	8.5	6.7	7.4
r	—	0.990	0.987	0.991	0.989

These values are higher than the ρ^+ value (5.6 kcal mol^{-1}) for the isolated X—C_6H_4—OH molecules in the gas phase. This means that the microsolvation model can also be used to interpret the experimental observations. Nevertheless, compared with Bordwell *et al.*'s (8.1 kcal mol^{-1}) and Lind *et al.*'s (8.3 kcal mol^{-1}) ρ^+ values, these ρ^+ values are lower by about 1 kcal mol^{-1}. Therefore, the microsolvation model is not adequate either.

Semi-continuum solvation

Better descriptions of solvation effects can often be achieved when one combines the implicit solvation model with the explicit solute–solvent complexation model (for some recent applications of the semi-continuum solvation model, see Ref. 18). Using this 'semi-continuum' approach, one can describe the long-range solvation effects using the computationally less demanding continuum solvation model. At the same time, one can also take some of the first solvation shell interactions into account.

Using the semi-continuum approach, one can design the following reaction to model the real events happening in the aqueous solution for the phenol homolysis:

$$\begin{aligned} &X\text{-}C_6H_4\text{-}OH\cdots H_2O\,(\text{in solution}) \\ &\rightarrow X-C_6H_4\text{-}O^{\bullet}\cdots H_2O\,(\text{in solution}) + H^{\bullet}(\text{in solution}) \end{aligned} \tag{6}$$

In this model, the free energy of X—C_6H_4—OH$\cdots H_2O$ (in solution) or X—C_6H_4—O$^{\bullet}\cdots H_2O$ (in solution) can be calculated using the B3LYP–PCM method for the whole complex in a certain solution without any problem. However, currently we are not sure about how to calculate the solvation energy of H$^{\bullet}$ radical in an *ab initio* fashion. (Certainly one can use theoretical results from Eqn (6) and solution-phase experimental results for the O—H BDE of phenol to 'calculate' the solvation free energy of H$^{\bullet}$. Using this particular solvation energy and results in Table 4, one can also easily calculate the O—H BDEs for all the substituted phenols in the solution.) Fortunately, only the substituent effect on the reaction of Eqn (6) is needed in the present study. As a result, we can still easily calculate the relative O—H BDEs of the X—C_6H_4—OH$\cdots H_2O$ complexes in water. The results are given in Table 4. Similar results for the relative O—H BDEs of the X—C_6H_4—OH$\cdots$DMSO complexes in DMSO are also shown in Table 4.

According to Table 4, the ρ^+ value for the solution-phase BDEs of X—C_6H_4—OH$\cdots H_2O$ complexes is 8.5 kcal mol^{-1}. This value is in good agreement with Lind *et al.*'s ρ^+ value (8.3 kcal mol^{-1}) obtained from aqueous-phase measurements. Also, the theoretical ρ^+ value for the solution-phase BDEs of X—C_6H_4—OH$\cdots$ DMSO complexes is 7.4 kcal mol^{-1}. This value is lower than Bordwell *et al.*'s ρ^+ value (8.1 kcal mol^{-1}) by only 0.7 kcal mol^{-1}. At this point, it is pleasing that the experimental observations have finally been reasonably reproduced using the theoretical approach.

CONCLUSION

We have shown the importance of solvation effects on the O—H BDEs of substituted phenols. We demonstrated that the BDEs measured in solution do not in general equal the BDEs in the gas phase. A detailed theoretical analysis indicated that a long-range solvation effect (i.e. the interaction between the solvent and the overall dipole moment of the solute) and a short-range solvation effect (i.e. the hydrogen bonding between the solute and solvent) are both important for the O—H BDEs in water and in DMSO. Neither of these two factors by itself can fully explain the experimentally observed solvation effect. However, a combination of these two factors using a semi-continuum solvation model is reasonably successful in doing so.

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REFERENCES

1. (a) Denisov ET, Denisova TG (eds). *Handbook of Antioxidants* (2nd edn). CRC Press: Boca Raton, FL, 2000; (b) Zhu Q, Zhang X-M, Fry AJ. *Polym. Degrad. Stab.* 1997; **57**: 43; (c) Borges dos Santos RM, Martinho Simoes JA. *J. Phys. Chem. Ref. Data* 1998; **27**: 707; (d) Zhang HY, Chen DZ. *Chin. Chem. Lett.* 2000; **11**: 727; (e) Zhang HY, Sun YM, Chen DZ. *Chin. Chem. Lett.* 2001; **12**: 75; (f) Pedulli GF, Lucarini M. *Trends Org. Chem.* 2001; **9**: 97; (g) Fujisawa S, Atsumi T, Kadoma Y, Sakagami H. *Toxicology* 2002; **177**: 39; (h) Zhao B. *Chin. Sci. Bull.* 2003; **48**: 315.
2. (a) Mahoney LR, DaRooge MA. *J. Am. Chem. Soc.* 1975; **97**: 4722; (b) Bordwell FG, Cheng JP, Harrelson JA Jr. *J. Am. Chem. Soc.* 1988; **110**: 1229; (c) Mulder P, Saastad OW, Griller D. *J. Am. Chem. Soc.* 1988; **110**: 4090; (d) Lind J, Shen X, Eriksen TE, Merenyi G. *J. Am. Chem. Soc.* 1990; **112**: 479; (e) Bordwell FG, Cheng J, Ji GZ, Satish AV, Zhang X. *J. Am. Chem. Soc.* 1991; **113**: 9790; (f) Bordwell FG, Zhang X-M, Satish AV, Cheng J-P. *J. Am. Chem. Soc.* 1994; **116**: 6605; (g) Bordwell FG, Zhang X-M. *J. Phys. Org. Chem.* 1995; **8**: 529; (h) Lucarini M, Pedrielli P, Pedulli GF, Cabiddu S, Fattuoni C. *J. Org. Chem.* 1996; **61**: 9259; (i) de Heer MI, Korth H-G, Mulder P. *J. Org. Chem.* 1999; **64**: 6969; (j) Brigati G, Lucarini M, Mugnaini V, Pedulli GF. *J. Org. Chem.* 2002; **67**: 4828.
3. (a) Wu Y-D, Lai DKW. *J. Org. Chem.* 1996; **61**: 7904; (b) Brinck T, Haeberlein M, Jonsson M. *J. Am. Chem. Soc.* 1997; **119**: 4239; (c) Zhang H-Y, Chen D-Z. *Chin. J. Org. Chem.* 2001; **21**: 66; (d) Pratt DA, de Heer MI, Mulder P, Ingold KU. *J. Am. Chem. Soc.* 2001; **123**: 5518; (e) Sun Y-M, Zhang H-Y, Chen D-Z. *Chin. J. Chem.* 2001; **19**: 657; (f) Bean GP. *Tetrahedron* 2002; **58**: 9941. (g) Bosque R, Sales J. *J. Chem. Inf. Comput. Sci.* 2003; **43**: 637; (h) Zhang H-Y. *New J. Chem.* 2003; **27**: 453; (i) Zhang H-Y, Sun Y-M, Wang X-L. *Chem. Eur. J.* 2003; **9**: 502.
4. Pedrielli P, Pedulli GF. *Gazz. Chim. Ital.* 1997; **127**: 509.
5. Laarhoven LJJ, Mulder P, Wayner DDM. *Acc. Chem. Res.* 1999; **32**: 342.

6. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb A, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE Jr, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.7*. Gaussian: Pittsburgh, PA, 1998.
7. Henry DJ, Parkinson CJ, Mayer PM, Radom L. *J. Phys. Chem. A.* 2001; **105**: 6750.
8. (a) Cheng Y-H, Zhao X, Song K-S, Liu L, Guo Q-X. *J. Org. Chem.* 2002; **67**: 6638; (b) Song K-S, Liu L, Guo Q-X. *J. Org. Chem.* 2003; **68**: 262; (c) Lin B-L, Fu Y, Liu L, Guo Q-X. *Chin. Chem. Lett*. 2003; **14**: 1073.
9. Boys SF, Bernardi F. *Mol. Phys.* 1970; **19**: 553.
10. (a) Tomasi J, Persico M. *Chem. Rev.* 1994; **94**: 2027; (b) Barone V, Cossi M, Tomasi J. *J. Chem. Phys.* 1997; **107**: 3210.
11. Smith DM, Buckel W, Zipse H. *Angew. Chem., Int. Ed. Engl.* 2003; **42**: 1867.
12. Pliego JR, Riveros JM. *Chem. Phys. Lett.* 2002; **355**: 543.
13. Bondi A. *J. Phys. Chem.* 1964; **68**: 441.
14. Bell RP. *Trans. Faraday Soc.* 1931; **27**: 797.
15. Cramer CJ, Truhlar DG. *Chem. Rev.* 1999; **99**: 2161.
16. (a) Lucarini M, Mugnaini V, Pedulli GF. *J. Org. Chem.* 2002; **67**: 928; (b) Fang Y, Liu L, Feng Y, Li X-S, Guo Q-X. *J. Phys. Chem. A* 2002; **106**: 4669; (c) Foti MC, Barclay LRC, Ingold KU. *J. Am. Chem. Soc.* 2002; **124**: 12881; (d) Korth H-G, de Heer MI, Mulder P. *J. Phys. Chem. A* 2002; **106**: 8779; (e) Do Couto PC, Guedes RC, Cabral BJC, Simoes JAM. *Int. J. Quantum Chem.* 2002; **86**: 297; (f) Zhang HY, Sun YM, Chen DZ. *Chin. Chem. Lett.* 2002; **13**: 531; (g) Zhang HY, Sun YM, Wang LF. *Chin. Chem. Lett.* 2003; **14**: 209; (h) Aloisio S, Francisco JS. *J. Phys. Chem. A* 2003; **107**: 2492; (i) Guedes RC, Coutinho K, Costa CBJ, Canuto S. *J. Phys. Chem. B* 2003; **107**: 4304.
17. Desiraju GR. *Acc. Chem. Res.* 1991; **24**: 290.
18. (a) Pliego JR, Riveros JM. *J. Phys. Chem. A* 2002; **106**: 7434; (b) Tomasi J, Cammi R, Mennucci B, Cappelli C, Corni S. *Phys. Chem. Chem. Phys.* 2002; **4**: 5697; (c) Musaev DG, Hirao K. *J. Phys. Chem. A* 2003; **107**: 1563; (d) Lopez X, Mujika JI, Blackburn GM, Karplus M. *J. Phys. Chem. A* 2003; **107**: 2304.
19. Hansch C, Leo A, Taft RW. *Chem. Rev.* 1991; **91**: 165.

