Critical Re-evaluation of the O−H Bond Dissociation Enthalpy in Phenol

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Received: June 30, 2004; In Final Form: December 16, 2004

The gas-phase O−H bond dissociation enthalpy, BDE, in phenol provides an essential benchmark for calibrating the O−H BDEs of other phenols, data which aids our understanding of the reactivities of phenols, such as their relevant antioxidant activities. In a recent review, the O−H BDE for phenol was presented as 90 ± 3 kcal mol^{-1} (*Acc. Chem. Res.* **2003**, *36*, 255−263). Due to the large margin of error, such a parameter cannot be used for dynamic interpretations nor can it be used as an anchor point in the development of more advanced computational models. We have reevaluated the existing experimental gas-phase data (thermolyses and ion chemistry). The large errors and variations in thermodynamic parameters associated with the gas-phase ion chemistry methods produce inconsistent results, but the thermolytic data has afforded a value of 87.0 ± 0.5 kcal mol^{-1}. Next, the effect of solvent has been carefully scrutinized in four liquid-phase methods for measuring the O−H BDE in phenol: photoacoustic calorimetry, one-electron potential measurements, an electrochemical cycle, and radical equilibrium electron paramagnetic resonance (REqEPR). The enthalpic effect due to solvation, by, e.g., water, could be rigorously accounted for by means of an empirical model and the difference in hydrogen bond interactions of the solvent with phenol and the phenoxyl radical. For the REqEPR method, a second correction is required since the calibration standard, the O−H BDE in 2,4,6-tri-*tert*-butylphenol, had to be revised. From the gas-phase thermolysis data and three liquid-phase techniques (excluding the electrochemical cycle method), the present analysis yields a gas-phase BDE of 86.7 ± 0.7 kcal mol^{-1}. The O−H BDE was also estimated by state-of-the-art computational approaches (G3, CBS-APNO, and CBS-QB3) providing a range from 86.4 to 87.7 kcal mol^{-1}. We therefore recommend that in the future, and until further refinement is possible, the gas-phase O−H BDE in phenol should be presented as 86.7 ± 0.7 kcal mol^{-1}.

The pivotal physical property of a covalent bond is its bond dissociation enthalpy (BDE), a term which refers strictly to three relevant species being in the gas phase at 298 K and at the thermodynamic standard state of 1 atm. BDEs determine the rates of homolytic bond cleavage reactions such as unimolecular thermolyses of peroxide initiators and bimolecular atom transfers. When these thermodynamic quantities are known with sufficiently high accuracy they become an invaluable tool for predicting homolytic reaction rates and validating proposed reaction mechanisms. As a result of refinement, adjustment, recalibration, and reanalyses of experimental data plus an improved understanding of the physics of the chemical bond, the BDEs for many prototypical compounds have been revised, often dramatically, over time. For example, during the past half century or so, the C−H BDE in benzene, C_6H_5−H, was increased from 103[1] to 112.9[2] kcal mol^{-1} and that in toluene, $C_6H_5CH_2$−H, was increased from 77.5[3] to 89.7[2] kcal mol^{-1}. Nevertheless, as a recent review[2] demonstrates, the number of reliable BDEs with error margins of 0.5 kcal mol^{-1} or less is quite limited. In this respect, it is astonishing that the O−H BDE in phenol, a benchmark aromatic alcohol, has been tabulated as 90 ± 3 kcal mol^{-1}.[2]

The O−H BDEs for phenols, both natural, e.g., α-tocopherol (vitamin E), and synthetic, e.g., 2,6-di-*tert*-butyl-4-methylphenol (BHT), are of considerable importance because these compounds provide a vital defense against unwanted aerial oxidation in living organisms and commercial products, respectively. The antioxidant activities of phenols arise from their ability to trap chain-carrying peroxyl radicals by donating their phenolic hydrogen atom,[4] e.g., eq 1. The kinetics and thermodynamics for this reaction are intimately related

$$C_6H_5OH + ROO^\bullet \rightarrow C_6H_5O^\bullet + ROOH \qquad (1)$$

Accordingly, an accurate prediction of the heat of reaction, Δ_rH_1, is a prerequisite for assessing the antioxidant activities of phenols in a quantitative manner.

In a 1995 publication[5] describing the measurement of the O−H BDE in phenol by photoacoustic calorimetry (PAC), we

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10.1021/jp047148f CCC: $30.25

TABLE 1: Summary of Post-1994 Experimental Values for the O−H BDE in Phenol (kcal mol^{-1}, 298 K)

year	method	solvent	O−H BDE	ref.
1995	photoacoustic calorimetry	various	87.3	5, 6
1996	radical equilibrium EPR	benzene	88.3 ± 0.8	7
1996	electrochemical cycle	DMSO	90.4 ± 1.0	8
1998	negative ion cycle	none	90 ± 3	9a
2000	proton affinity cycle	none	91 ± 1	10
2004	negative ion cycle	none	85.8 ± 1.9	9b

included a table of the 10 then available literature values for this quantity. Half of these literature values had been derived, using a variety of experimental procedures, from measurements in the liquid phase and half from measurements in the gas phase. The range in O−H BDEs was impressive, viz. 84.0−91.6 kcal mol^{-1}, whereas the mean of our own measured values in five different solvents was 87.3[5,6] kcal mol^{-1}. Table 1 demonstrates that the situation regarding experimental measurements of the O−H BDE in phenol has hardly improved since 1995, i.e., still spanning a range from 85.8 to 91 kcal mol^{-1}.[6−10] Indeed, accepting a direct relationship between the enthalpy of activation, E_{a1}, and ΔH_1, such a range implies an uncertainty in the rate for reaction 1 of about 6500 at 298 K.

The diversity in O−H BDEs shown in Table 1 reflects, in part, the fact that for each methodology the final BDE is computed using auxiliary physical data, which may be of variable quality. In addition, values derived from experimental measurements in the liquid phase may be in error because of failures to make the proper corrections for hydrogen bond formation between the phenol (hydrogen donor) and solvent (hydrogen acceptor). Insufficient allowance for the effects of hydrogen bonding causes the purported “gas-phase” O−H BDEs for phenol to be larger, sometimes by several kcal mol^{-1}, than the correct values as we have documented in earlier publications.[5,11]

In view of its importance and the current uncertainty (Table 1), we have undertaken a systematic study of the O−H BDE in phenol by collecting and re-evaluating all of the experimental data and by performing some high-level computations. The result is a refined, gas-phase, O−H BDE with an acceptable margin of error.

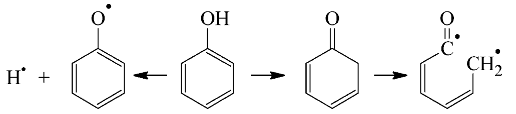
Results and Discussion

Gas-Phase Kinetic Studies. The most direct approach to determine the O−H BDE of phenol in the gas-phase would be to study the temperature dependence of the homolytic O−H bond cleavage reaction, eq 2

$$C_6H_5OH \rightarrow C_6H_5O^\bullet + H^\bullet \tag{2}$$

The value of Δ_rH_2, or the O−H BDE, at 298 K could then be obtained from the experimentally determined activation enthalpy. This approach has been successfully utilized to establish the benzylic C−H BDE in toluene. However, for phenol, such an endeavor cannot be successful due to the presence of a competing (gas-phase) tautomerization of phenol to cyclohexa-2,4(2,5)-dienone. The thermal degradation of the 2,4-tautomer sets in with a C−C bond rupture, which obscures the kinetics of the homolytic O−H bond cleavage, Scheme 1.[12]

SCHEME 1



An indirect way to assess the O−H BDE is by studying the temperature dependence of the rate for O−C bond homolysis in phenyl ethers, eq 3,

$$C_6H_5OR \rightarrow C_6H_5O^\bullet + R^\bullet \tag{3}$$

and combining the kinetic results with auxiliary thermodynamic data. The choice of R is, however, limited since a four-centered elimination (eq 4) may compete with O−R bond homolysis when R contains a β-C−H bond which convolutes the kinetic information.[13] Only for R = CH_3, C_6H_5, or $C_6H_5CH_2$ will homolysis of the O−R bond be the unique route for thermal decomposition.

$$C_6H_5OCH_2CH_3 \rightarrow C_6H_5OH + C_2H_4 \tag{4}$$

The results of gas-phase thermolytic studies on anisole and diphenyl ether are summarized in Table 2. Results for C−C fragmentation of ethylbenzene are also included for comparison (eq 5). There is a remarkably good agreement between the experimental E_as from four independent studies on anisole and these E_a values have been converted into Δ_rH (= BDE) at 298 K using a restricted Gorin transition state model and eq 6[17]

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2^\bullet + CH_3^\bullet \tag{5}$$

$$\mathrm{BDE(O{-}C)} = E_a + RT_m - \Delta\overline{Cp}\,(T_m - 298) \tag{6}$$

In this equation, T_m is the average temperature of the experiment, $\Delta\overline{Cp}$ is the average change in heat capacity between T_m and 298 K (see footnote b of Table 2). These experimental results yield an average O−CH_3 BDE in anisole of 65.3 ± 0.4 kcal mol^{-1}, an O−C_6H_5 BDE in diphenyl ether of 79.8 kcal mol^{-1}, and a C−CH_3 BDE in ethylbenzene of 77.7 kcal mol^{-1}, all at 298 K (Table 2). The O−H BDE in phenol can now be extracted from these O−C BDEs using eqs 7 and 8

TABLE 2: Activation Parameters and BDE(O−C/C−C) (in kcal mol^{-1} at 298 K) for Homolytic Bond Cleavage in Anisole, Ethylbenzene, and Diphenyl Ether

compound	method[a]	temp range (K)	E_a	log(A/s^{-1})	T_m (K)	$E_a + RT_m$	BDE(O−C)[b] (C−C)	ref
$C_6H_5O-CH_3$	TC	790−900	63.6	15.3	845	65.3	64.8	14a
$C_6H_5O-CH_3$	LP	850−1000	64.0	15.5	925	65.8	65.5	14b
$C_6H_5O-CH_3$	VLPP	900−1100	63.9	15.3	1000	65.9	65.7	14c
$C_6H_5O-CH_3$	VLPP	900−1150	63.5	15.4	1025	65.5	65.4	14d
$C_6H_5CH_2-CH_3$	various	770−1800	75.1	15.8	1285	77.7	77.7	15
$C_6H_5O-C_6H_5$	VLPP	1000−1200	75.7	15.5	1100	77.9	79.8	16

[a] TC: toluene carrier method; LP: low-pressure pyrolysis; VLPP: very low-pressure pyrolysis. [b] With eq 6, and $\Delta\overline{Cp}$ (in cal mol^{-1}K^{-1}) of 0.86, 0.56, 0.30, 0.22 ($C_6H_5OCH_3$), −0.01 ($C_6H_5CH_2CH_3$), and −2.40 ($C_6H_5OC_6H_5$) as computed at the B3LYP/6-31G(d,p)// B3LYP/6-31G(d,p) level between T_m and 298 K.

$$\mathrm{BDE(O{-}C)} = \Delta_f H(\mathrm{C_6H_5O^\bullet}) + \Delta_f H(\mathrm{R^\bullet}) - \Delta_f H(\mathrm{C_6H_5OR}) \quad (7)$$

$$\mathrm{BDE(O{-}H)} = \Delta_f H(\mathrm{C_6H_5O^\bullet}) + \Delta_f H(\mathrm{H^\bullet}) - \Delta_f H(\mathrm{C_6H_5OH}) \quad (8)$$

in conjunction with auxiliary thermodynamic quantities (see also Table S1).[18] Taking $\Delta_f H(C_6H_5OCH_3) = -18.33$[19] kcal mol^{-1} yields the O−H BDE in phenol as 87.0 ± 0.4 kcal mol^{-1}, whereas the diphenyl ether data[20] yield an O−H BDE of 86.9 ± 0.6 kcal mol^{-1}. The kinetics for ethylbenzene thermolysis renders a C−H BDE in toluene of 89.8 ± 0.6 kcal mol^{-1}, in excellent agreement with the evaluated value[2] of 89.8 ± 0.6 kcal mol^{-1}, underscoring the consistency of these calculations.

Therefore, an O−H BDE in phenol of 87.0 ± 0.5 kcal mol^{-1} can be inferred from the gas-phase kinetic studies.

Gas-Phase Ion Cycle Studies.[21] One thermodynamic gas-phase method for the determination of the O−H BDE involves measurement of the acidity of phenol ($\Delta_{acid}H$), eq 9, the electron affinity (*EA*) of the phenoxyl radical, eq 10, and the ionization energy (*IE*) of the hydrogen atom, eq 11

$$\mathrm{C_6H_5OH} \rightarrow \mathrm{C_6H_5O^-} + \mathrm{H^+} \quad (9)$$

$$\mathrm{C_6H_5O^-} \rightarrow \mathrm{C_6H_5O^\bullet} + \mathrm{e^-} \quad (10)$$

$$\mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H^\bullet} \quad (11)$$

Combination of the thermodynamic parameters for the negative ion cycle yields the O−H BDE in phenol according to eq 12

$$\mathrm{BDE(O{-}H)} = \Delta_{acid}H(\mathrm{C_6H_5OH}) + EA(\mathrm{C_6H_5O^\bullet}) - IE(\mathrm{H^\bullet}) \quad (12)$$

With an average $\Delta_{acid}H$ for phenol of 350.4 ± 3.1,[18] an $EA(C_6H_5O^\bullet)$ of 51.95 ± 0.14,[22] and an $IE(H^\bullet)$ of 313.58,[18] eq 12 yields an O−H BDE of 88.7 ± 3.2 kcal mol^{-1}.[23] Recently, the $\Delta_{acid}H$ for phenol has been remeasured to be 347.5 ± 1.9,[9b] leading to an O−H BDE of 85.8 ± 1.9 kcal mol^{-1}.

Apparently, in gas-phase ion studies on phenol high error margins or uncertainties are encountered. This is rather surprising since for small organic molecules the errors in $\Delta_{acid}H$ are usually at or below 1 kcal mol^{-1}.

We have computed the parameters of eq 12 (Table 3) by the CBS-QB3 method (vide infra) and obtained an O−H BDE of 87.1 kcal mol^{-1} at 298 K.[24]

Another gas-phase ion cycle involves the ionization energy of phenol (*IE*), eq 13, and the proton affinity (*PA*) of the phenoxyl radical, eq 14, which are again used in conjunction with $IE(H^\bullet)$. Accordingly, the O−H BDE in phenol can be retrieved from eq 15

$$\mathrm{C_6H_5OH} \rightarrow \mathrm{C_6H_5OH^{\bullet+}} + \mathrm{e^-} \quad (13)$$

$$\mathrm{C_6H_5OH^{\bullet+}} \rightarrow \mathrm{C_6H_5O^\bullet} + \mathrm{H^+} \quad (14)$$

$$\mathrm{BDE(O{-}H)} = IE(\mathrm{C_6H_5OH}) + PA(\mathrm{C_6H_5O^\bullet}) - IE(\mathrm{H^\bullet}) \quad (15)$$

There appears to be a serious disagreement concerning the *PA* of the phenoxyl radical. The evaluated (recommended) value is 205.0,[18] but a *PA* of 208.7 ± 1.0 kcal mol^{-1} was recently reported at 298 K.[10] Thus, with the *IE*(phenol) = 195.8 ± 0.5,[18] the O−H BDE in phenol is either 87.2 ± 1.0 or 90.9 ± 1.0 kcal mol^{-1}! Our CBS-QB3 computations (see Table 3) yield a $PA(C_6H_5O^\bullet)$ which is 2−6 kcal mol^{-1} lower than the experiment.[24]

TABLE 3: Experimental and Computed Gas-Phase Ion Cycle Parameters (kcal mol^{-1})[a]

eq		CBS-QB3 (298 K)	exp	ref.
9	$\Delta_{acid}H(C_6H_5OH)$	348.72	350.4 ± 3.1	18
			347.5 ± 1.9	9b
10	$EA(C_6H_5O^\bullet)$	51.41	51.95 ± 0.14	22
11	$IE(H^\bullet)$	313.05	313.58	18
13	$IE(C_6H_5OH)$	197.48	195.8 ± 0.5	18
14	$PA(C_6H_5O^\bullet)$	202.66	205.0	18
			208.7 ± 1.0	10

[a] For additional computational details, see Table S2.

Gas-phase ion studies do not provide a consistent value for the O−H BDE in phenol. The experimental uncertainty is generally quite substantial.

Liquid-Phase Studies. *Enthalpies of Solvation Corrections.* To obtain the gas-phase $C_6H_5O{-}H$ BDE from measurements in solution it is essential to correct for the enthalpy of solvation of C_6H_5OH, $C_6H_5O^\bullet$ and $H^\bullet$. By definition, the relationship between $\mathrm{BDE}(C_6H_5O{-}H)^{gas}$ and $\mathrm{BDE}(C_6H_5O{-}H)^{sol}$ in solvent, A, simply requires subtraction from the latter of the enthalpy of solvation of the hydrogen atom and the difference in the enthalpies of solvation of the phenoxyl radical and of phenol, i.e.

$$\mathrm{BDE}(\mathrm{C_6H_5O{-}H})^{gas} = \mathrm{BDE}(\mathrm{C_6H_5O{-}H})^{A} - \Delta_{solv}H\,(\mathrm{H^\bullet})^{A} - (\Delta_{solv}H\,(\mathrm{C_6H_5O^\bullet})^{A} - \Delta_{solv}H(\mathrm{C_6H_5OH})^{A}) \quad (16)$$

In eq 16, $\mathrm{BDE}(C_6H_5O{-}H)^{gas}$ refers to the standard concentration state of 1 M, whereas BDEs obtained from gas-phase experiments (through eq 6) and from computational studies, use 1 atm as the thermodynamic standard state. These two quantities are related, eq 17, to one another as

$$\mathrm{BDE\ (1\ atm)} = \mathrm{BDE\ (1\ M)} + RT(1\text{-}\alpha T) \quad (17)$$

with α as the isobaric thermal expansivity coefficient of the solvent.[25a] For the organic solvents used in this study, α is about 1.2 kK^{-1}; hence, BDE (1 atm) = BDE (1 M) + 0.4 kcal mol^{-1} at 298 K.[25b]

The enthalpy of solvation of $H^\bullet$ is relatively constant in solvents as varied as isooctane, benzene, chlorobenzene, acetonitrile, dimethyl sulfoxide, and *N*,*N*-dimethylformamide with an average value of 2 ± 0.5 kcal mol^{-1}.[26] The $\mathrm{BDE}(C_6H_5O{-}H)^{A}$ in eq 16 is obtained from experimental enthalpic data (vide infra) and depends also on the assumption for $\Delta_{solv}H(H^\bullet)^{A}$. It is of no consequence for the $\mathrm{BDE}(C_6H_5O{-}H)^{gas}$ in eq 16 which value for $\Delta_{solv}H(H^\bullet)^{A}$ is selected since it cancels out. The major and generally the only significant difference between $\Delta_{solv}H(C_6H_5OH)^{A}$ and $\Delta_{solv}H(C_6H_5O^\bullet)^{A}$ is due to hydrogen bond formation between the phenol and the solvent (eq 18) if the latter is a hydrogen bond acceptor (HBA)

$$\mathrm{C_6H_5OH} + \mathrm{A} \rightleftharpoons \mathrm{C_6H_5OH{-}{-}{-}A} \quad (18)$$

This leads to a simple relationship between the bond enthalpies in the gas-phase and in solution (eq 19) where $\Delta_r H^{A}_{18}$ is the enthalpy of the hydrogen bond[5]

$$\mathrm{BDE}(\mathrm{C_6H_5O{-}H})^{gas} = \mathrm{BDE}(\mathrm{C_6H_5O{-}H})^{A} - \Delta_{solv}H(\mathrm{H^\bullet})^{A} + \Delta_r H(\mathrm{C_6H_5OH{-}{-}{-}A})^{A}_{18} \quad (19)$$

There is very good evidence that a phenol molecule can act as a hydrogen bond donor (HBD) to only a single HBA molecule, A, at any one time and that the magnitude of the equilibrium constant, K_{18}^{A}, and hence of the enthalpy of the hydrogen bond, $\Delta_r H(C_6H_5OH\text{- - -}A)_{18}^{A}$, is essentially independent of the surrounding properties (e.g., the medium dielectric constant).[11,27] It is therefore immaterial whether $\Delta_r H_{18}^{A}$, or K_{18}^{A}, have been determined in the pure HBA solvent, A, or, as is more usual for K_{18}^{A}, in CCl_4 containing relatively low concentrations of PhOH and A. To calculate BDE($C_6H_5O{-}H$)^{gas} from measurements made in solution, the best value of $\Delta_r H$ $(C_6H_5OH\text{- - -}A)_{18}^{A}$ can be obtained from literature sources.[28] If neither $\Delta_r H_{18}^{A}$ nor K_{18}^{A} have been reported for the solvent in question, Abraham et al.'s[29] empirical eq 20 can be employed to estimate K_{18}^{A}

$$\log K_{18}^{A} = 7.354\,\alpha_2^{H}\beta_2^{H} - 1.094 \qquad (20)$$

In eq 20 the equilibrium constant, K_{18}^{A}, for 1:1 complexation in CCl_4 at room temperature between a hydrogen bond donor (HBD) solute and a HBA solute is calculated from the HBD and HBA activities of the two solutes, as given by Abraham et al.'s α_2^{H} and β_2^{H} scales, respectively.[30,31] For phenol α_2^{H} = 0.596[30] and β_2^{H} values are available for several hundred HBAs.[31] Abraham's compilation afford log K_{18}^{A}, or $\Delta_r G_{18}$, for the formation of a 1:1 complex. Independently, Arnett et al. have determined a vast number of hydrogen bond enthalpies, $\Delta_r H_{18}$, by a calorimetric method (the pure base-method).[28b] The differences in solvation enthalpies, between e.g. phenol and anisole, in various bases have been attributed to the hydrogen bonding enthalpies.[28b] When combining the two data sets for phenol and 4-F-phenol and 21 bases (DMSO not included) a linear ($r^2 = 0.963$) relationship emerges, eq 21

$$\Delta_r H_{18}/\text{kcal mol}^{-1} = (\Delta_r G_{18} - 1203.6)/0.487 \qquad (21)$$

The mean unsigned deviation between $\Delta_r H_{18}$ as calculated by eq 21, and the original experimental enthalpic information from Arnett et al. is 0.4 kcal mol^{-1} with $n = 42$. After rearranging eq 21, eq 22 is obtained in which the $\Delta_r H_{18}$ is directly related to α_2^{H} and β_2^{H}. This equation allows the computation of the hydrogen bond enthalpy for any combination of a (phenolic) solute and a neat solvent with an accuracy of ±0.4 kcal mol^{-1}.[32]

$$\Delta_r H_{18}/\text{kcal mol}^{-1} = -20.56\,\alpha_2^{H}\,\beta_2^{H} + 0.59 \qquad (22)$$

Methods. Four liquid-phase experimental methods have produced benchmark BDE($C_6H_5O{-}H$) values, three of which are in rather satisfactory agreement with the 87.0 ± 0.5 kcal mol^{-1} derived from gas-phase kinetic studies (vide supra).

(i) Photoacoustic Calorimetry (PAC).[33] In this technique, the enthalpy deposited in solution $\Delta_r H$, is measured after very rapid photodissociation of the O−O bond in di-*tert*-butyl peroxide using a pulse from a nitrogen laser (337 nm) in the presence of phenol, eqs 23 and 24

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2\,(CH_3)_3CO^{\bullet} \qquad (23)$$

$$(CH_3)_3CO^{\bullet} + C_6H_5OH \rightarrow (CH_3)_3COH + C_6H_5O^{\bullet} \qquad (24)$$

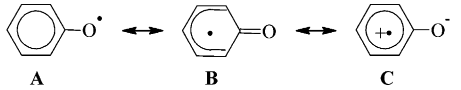
Deriving accurate BDEs by PAC is beset by problems, such as the variation in the quantum yield for peroxide photolysis in different solvents, but all these difficulties can be overcome.[5,6] The experimental values of $\Delta_r H$ also depend, of course, on the HBA activities (β_2^{H} values) of the solvent. Measurements were made in five solvents[5] and the following corrected[6] $C_6H_5O{-}H$ BDEs (in kcal mol^{-1}) were obtained in isooctane 86.1 (0.0), CCl_4 88.0 (0.0), benzene 86.0 (1.2), acetonitrile 88.1 (4.9), ethyl acetate 88.1 (4.9), where the numbers in parentheses correspond to $\Delta_r H(C_6H_5OH\text{- - -}A)_{18}^{A}$ according to eq 22. In a later study,[33b] and after some experimental improvements, three PAC measurements were repeated and reanalysis (eq 22) yields $C_6H_5O{-}H$ BDEs in kcal mol^{-1} of 86.3 (isooctane), 86.0 (benzene), and 86.3 (ethyl acetate).[33b] It was also found that in CCl_4 a UV red-shift of the phenol absorbance occurred, which hampers a reliable PAC determination.[33b] A typical PAC experiment consists of measuring the linear relation between the photoacoustic signal and the transmission (1-T) of a solution by varying the concentration (up to ca. 1 M) of the light-absorbing di-*tert*-butyl peroxide.[33a] The slope of the graph is proportional to the heat released in solution. In all of the PAC work on phenol, it was tacitly assumed that di-*tert*-butyl peroxide did not form a hydrogen bond with phenol (eq 18). However, this assumption is not justified because di-*tert*-butyl peroxide has being reported to have a β_2^{H} of 0.33,[31b] a value which we have confirmed by the usual infrared spectroscopic method.[31] This prompted us to scrutinize the enthalpic effect on the PAC results arising from the variable amount of di-*tert*-butyl peroxide present in solution. Data for the binary solvent systems (isooctane, benzene, or ethyl acetate mixed with di-*tert*-butyl peroxide) are presented in Tables S3 and S4 (see Supporting Information). The enthalpic contribution by hydrogen bonding between phenol and di-*tert*-butyl peroxide is most strongly manifested in the non-HB solvent isooctane. In a PAC experiment, the influence on the PAC signal, due to hydrogen bonding by di-*tert*-butyl peroxide, is a nonlinear phenomenon, since the solution's transmission is used rather than the absorbance.[33] However, based on experience, the regression coefficients for linearity between the magnitude of the PAC response and 1-T were always better than 0.999. Without seeking a mathematical solution, we use the $\Delta_r H(C_6H_5OH\text{- - -}A)_{18}^{A}$ at an average concentration of 0.5 M of di-*tert*-butyl peroxide (see Table S4) to correct our earlier data. The $C_6H_5O{-}H$ BDEs in kcal mol^{-1} now become 85.6 (isooctane), 85.7 (benzene), and 86.3 (ethyl acetate). Thus, in the non-HBA solvent, isooctane ($\beta_2^{H} = 0.00$),[31a] the weak HBA solvent benzene ($\beta_2^{H} = 0.15$),[31a] and the strong HBA solvent ethyl acetate ($\beta_2^{H} = 0.45$),[31a] the $C_6H_5O{-}H$ BDE value, including the inherent error limit for PAC experiments, is 85.9 ± 1.0 kcal mol^{-1} (1 M standard state), or 86.3 ± 1.0 kcal mol^{-1} (1 atm standard state, see eq 17).

(ii) One-Electron Reduction Potential of the Phenoxyl Radical in Water Combined with the Aqueous Acidity of Phenol ($E°$/pK_a).[34] In principle, one-electron redox potentials ($E°$) can be obtained by electrochemical methods, such as cyclic voltammetry. However, reliable data require a reversible, or quasi-reversible, process and a reasonable lifetime for the phenoxyl radical. These conditions are not met by the $C_6H_5O^{\bullet}/C_6H_5O^{-}$ couple because the $C_6H_5O^{\bullet}$ radical is more easily oxidized than the $C_6H_5O^{-}$ anion and the second oxidation step will be followed by irreversible hydrolysis to form hydroquinones. Moreover, at high current densities, the $C_6H_5O^{\bullet}$ radicals will undergo their very rapid dimerization reactions.

The above-mentioned difficulties have been overcome by Lind et al.[34] Pulse radiolysis was employed to generate $C_6H_5O^{\bullet}$ from $C_6H_5O^{-}$ in water at high pH. Use was then made of the rapidly established equilibrium between the $C_6H_5O^{\bullet}$/ $C_6H_5O^{-}$ couple and various reliable reference pairs, such as $ClO_2^{\bullet}/ClO_2^{-}$, to “anchor” $E°(C_6H_5O^\bullet)$ relative to the NHE (and referring to 1 atm of hydrogen). Rate and equilibrium constants for the various reactions were measured by UV/vis absorption spectroscopy. Combination of $E°(C_6H_5O^\bullet)$ and $pK_a(C_6H_5OH)$ yielded $\Delta_rG_{25}°$ from which $BDE(C_6H_5O-H)^{aq}$ was calculated to be 88.2 ± 0.3 kcal mol^{-1}, which was stated to be a “safe upper limit” for $BDE(C_6H_5O-H)^{gas}$.[34]

$$C_6H_5OH(aq) \rightarrow C_6H_5O^\bullet(aq) + {}^1/_2H_2(gas) \qquad (25)$$

To convert Lind et al.’s[34] $BDE(C_6H_5O-H)^{aq}$ to $BDE(C_6H_5O-H)^{gas}$, it is not necessary to correct for the heat of solvation of the hydrogen atom because the measurements directly link molecular gaseous hydrogen (and the dissolved proton) with the $C_6H_5O^\bullet$/ C_6H_5OH couple in solution. However, it is necessary to correct for the difference in the heats of solvation of C_6H_5OH and $C_6H_5O^\bullet$. The former will be the greater because of hydrogen bonding from the phenol to water. The β_2^H for water is 0.38,[31a] and therefore, according to eq 22, $\Delta_rH(C_6H_5OH\text{- - -}OH_2)_{18}^{water} = -4.1$ kcal mol^{-1}. The assumption that the enthalpy of solvation of the $C_6H_5O^\bullet$ radical is approximately the same as the enthalpy of solvation of the C_6H_5O moiety of C_6H_5OH is probably true for most organic solvents. However, this assumption is likely to be invalid in water, because the calculated (by QCISD/6-311G(d,p)) dipole moment for the phenoxyl radical (3.45 D) is significantly larger than the calculated dipole moment for phenol (1.34 D; exp:1.224 ± 0.008 D[35]) and anisole (1.33 D; exp:1.38 ± 0.07 D[35]). The large dipole moment for $C_6H_5O^\bullet$ can be understood in terms of delocalization. That is, the contributions of resonance structures **B** and **C** make phenoxyl more of a delocalized carbon-centered radical than a localized oxygen-centered radical, **A**,[36a] the $O^\bullet$ moiety being a strong EW group.[36b]



The high dielectric constant of water ($\epsilon = 78.5$) suggests, therefore, that $C_6H_5O^\bullet$ will have a significantly larger solvation enthalpy than the C_6H_5O moiety of C_6H_5OH (or C_6H_5OMe). Since the phenoxyl radical can be considered as a carbon-centered radical (**B**, **C**), the $\Delta_{solv}H(C_6H_5O^\bullet)^{aq}$ can be estimated by considering the interaction of the carbonyl moiety as the hydrogen bond acceptor and water as the hydrogen bond donor. With $\alpha_2^H(H_2O) = 0.353$[30] and $\beta_2^H(RC(O)R) = 0.48$,[31a] eq 22 predicts $\Delta_rH(C_6H_5O^\bullet\text{- - -}HOH)_{18}^{aq} = -2.9$ kcal mol^{-1}. Consequently, $\Delta_rH(C_6H_5OH\text{- - -}OH_2)_{18}^{aq} - \Delta_rH(C_6H_5O^\bullet\text{- - -}HOH)_{18}^{aq} = -4.1 - (-2.9) = -1.2$ kcal mol^{-1}.

Theoretical calculations have also been used in an attempt to quantify the effect of solvation on the phenol/phenoxyl couple. Thus, Guedes et al.[37] carried out Monte Carlo simulations and thermodynamic perturbation theory calculations to determine $\Delta_{solv}H(C_6H_5OH)^{aq} - \Delta_{solv}H(C_6H_5O^\bullet)^{aq}$. These workers found this difference to be about 8 kcal mol^{-1} which was explained on the basis that the enthalpy of HBD by phenol was greater than the enthalpy of HBA by phenoxyl. Almost identical results were obtained from a computational DFT-study employing water clustered species.[38] However, the magnitude of the calculated differences in the solvation enthalpies of C_6H_5OH and $C_6H_5O^\bullet$ in water appears to be much too large. Moreover, for the same species and applying the same Monte Carlo simulation procedure, identical $\Delta_{solv}H$ values were found for benzene and acetonitrile.[39] These results are especially confusing because the hydrogen bond between phenol and acetonitrile is much stronger than the one between phenol and benzene. Guedes et al.[37a] conclude that the $BDE(C_6H_5O-H)^{aq}$ will be greater than $BDE(C_6H_5O-H)^{gas}$ by 7 kcal mol^{-1}, later[37b] reduced to ca. 5 kcal mol^{-1}. Both values are incompatible with many other observations. For example, if even the difference of 5 kcal mol^{-1} is combined with the Lind et al.’s[34] “safe upper limit” value for the $BDE(C_6H_5O-H)^{aq}$, it would lead to a $BDE(C_6H_5O-H)^{gas}$ of 88.2−5 = 83.2 kcal mol^{-1} which is clearly many kcal mol^{-1} lower than all other measured and calculated values. A computational study by Guerra et al.[40] has shown that the solvation enthalpies for phenol and phenoxyl greatly depend on the organization of the surrounding water molecules. We also turned to theory and calculated free energies of solvation, $\Delta_{solv}G^{aq}$, for the relevant species using two continuum solvent models, but the results were not encouraging (see Table S5 of the Supporting Information). Therefore, we will make the reasonable assumption that $\Delta\Delta_{solv}H(C_6H_5OH - C_6H_5O^\bullet)^{aq} = \Delta_rH(C_6H_5OH\text{- - -}OH_2)_{18}^{aq} - \Delta_rH(C_6H_5O^\bullet\text{- - -}HOH)_{18}^{aq} = -1.2$ kcal mol^{-1} as predicted by eq 22 from which the result of Lind et al.[34] yields $BDE(C_6H_5O-H)^{gas} = 87.0 \pm 0.3$ kcal mol^{-1} (at 1 atm).

(iii) One Electron Oxidation Potential of the Phenoxide Anion in DMSO Combined with the Acidity of Phenol in DMSO. (E_{ox}/pK_a).[8,41,42] This work suffers from such serious deficiencies in methodology that it cannot be used to estimate a reliable value for $BDE(C_6H_5O-H)^{gas}$, despite claims to the contrary.[8] In the first place, $E_{ox}(C_6H_5O^-)$ was determined by cyclic voltammetry using peak potentials because the wave was irreversible.[41] Second, the value of $BDE(C_6H_5O-H)^{DMSO}$ was estimated to be 89.8[41] (later[8] 90.4) kcal mol^{-1} by using the empirical eq 26

$$BDE(C_6H_5O-H)^{DMSO}/\text{kcal mol}^{-1} = 1.37\ pK_a^{DMSO} + 23.06\ E_{ox}(C_6H_5O^-) + 73.3 \qquad (26)$$

The constant 73.3 in eq 26 had been obtained by plotting 1.37 pK_a + 23.06 E_{ox} against the gas-phase BDEs of fifteen weak, non-hydroxylic organic acids, mainly hydroaromatics.[43] In a broad criticism of the work described in ref 41 by some of the present authors,[5] it was pointed out that the constant in eq 26 could be calculated from literature data to be 76.2 and that the lower 73.3 value probably arose from its derivation using peak potentials uncorrected for homogeneous or heterogeneous kinetic effects. Furthermore, if $BDE(C_6H_5O-H)^{gas}$ actually was 87 kcal mol^{-1}, the measured value for $BDE(C_6H_5O-H)^{DMSO}$ should have been (see eq 19) 87 + $\Delta_{solv}H(H^\bullet)^{DMSO}$ + $\Delta_{solv}H(C_6H_5OH\text{- - -}DMSO)_{18}^{DMSO}$ = 87 + 2 + 7.2[28b] = 96.2 kcal mol^{-1}, not ca. 90 kcal mol^{-1} (at 1 M).

(iv) Radical Equilibrium Electron Paramagnetic Resonance (REqEPR). Foti et al.[44] reported that phenoxyl radicals abstract the phenolic hydrogen atom from other phenols remarkably rapidly. Building on this observation, Pedulli and co-workers [7,45,46] developed an EPR spectroscopic technique to measure the concentration ratio of two aryloxyl radicals, $ArO^\bullet$ and $Ar'O^\bullet$, under equilibrium conditions at known $ArOH/Ar'OH$ concentration ratios in benzene at room temperature, eq 27

$$ArO^\bullet + Ar'OH \rightleftharpoons ArOH + Ar'O^\bullet \qquad (27)$$

The REqEPR method yields Δ_rH_{27}, and hence the O−H BDEs under two assumptions: first, that $\Delta_rS_{27} = 0$;[47] second, that solvation effects for the two $ArO^\bullet/ArOH$ and $Ar'O^\bullet$/ $Ar'OH$ cancel. To convert these O−H ΔBDEs into BDEs, the O−H BDE in 2,4,6-tri-*tert*-butylphenol of 81.24 kcal mol^{-1} [49] was used as the reference. Using a series of three ArOH/ Ar′OH couples (C_6H_5OH/4-MeC_6H_4OH, 4-MeC_6H_4OH/2,6-$Me_2C_6H_3OH$ (alternatively: 4-MeC_6H_4OH/3,5-*t*-$Bu_2C_6H_3OH$) and 2,6-$Me_2C_6H_3OH$/2,4,6-*t*-$Bu_2C_6H_2OH$ (alternatively: 3,5-*t*-$Bu_2C_6H_3OH$/2,4,6-*t*-$Bu_3C_6H_2OH$)) the value found for BDE(C_6H_5O-H)^{benzene} was 88.3 ± 0.8 kcal mol^{-1}.[7]

Two corrections are required to convert the REqEPR BDE(C_6H_5O-H)^{benzene} to a BDE(C_6H_5O-H)^{gas} value. The first arises because the heat of formation of azobenzene has undergone revision. That is, the reference O−H BDE had been determined many years earlier by Mahoney et al.[49] using a direct calorimetric measurement of the heat of reaction for the oxidation of hydrazobenzene to *E*-azobenzene by the persistent 2,4,6-tri-*tert*-butylphenoxyl radical in benzene, eq 28

$$2\ t\text{-}Bu_3C_6H_2O^{\bullet} + C_6H_5NHNHC_6H_5 \rightarrow 2\ t\text{-}Bu_3C_6H_2OH + C_6H_5NNC_6H_5 \quad (28)$$

The heats of formation of *E*-azobenzene and hydrazobenzene in their standard states as solids were taken by Mahoney et al.[49] to be 76.49[50] and 52.9[51] kcal mol^{-1}, respectively. There have been no revisions to the heat of formation of hydrazobenzene. The heat of formation of *E*-azobenzene, however, has been remeasured three times 74.40 ± 0.81,[52] 73.76 ± 0.45,[53] and 74.43 ± 0.24[54] kcal mol^{-1}. Since there is no obvious reason to choose a "best value" from this series, we have simply used their medium value, viz., 74.20 kcal mol^{-1}. This leads us to suggest that *all* X−H BDEs based on the work of Mahoney et al.[49] should be adjusted downward by (76.49−74.20)/2 = 2.29/2 ≈ 1.1 kcal mol^{-1}, where the factor 1/2 arises because two hydrogen atoms are consumed for every molecule of *E*-azobenzene being produced from hydrazobenzene. Thus, BDE (2,4,6-*t*-$Bu_3C_6H_2O-H$)^{benzene} must be revised from its original value of 81.24 kcal mol^{-1} down to 80.1 kcal mol^{-1}. Consequently all the BDE(ArO−H)^{benzene} values measured by the REqEPR method must also be revised downward by 1.1 kcal mol^{-1} which would make BDE(C_6H_5O-H)^{benzene} = 88.3−1.1 = 87.2 ± 0.8 kcal mol^{-1}.

The second correction arises because the enthalpy for hydrogen bond formation to benzene by C_6H_5OH is greater than that for the sterically crowded 2,4,6-tri-*tert*-butylphenol. That is, irrespective of the choice of working couples relating the BDE(O−H)^{benzene} values for these two phenols, the value of $\Delta_r H_{29}$ for the overall equilibrium will be influenced by the difference in the HBD abilities of the two phenols

$$t\text{-}Bu_3C_6H_2O^{\bullet} + C_6H_5OH \rightleftharpoons t\text{-}Bu_3C_6H_2OH + C_6H_5O^{\bullet} \quad (29)$$

The shape and the size of the HBA molecule is a very important factor for H-bond formation by 2.6-di-*tert*-butylphenols.[55] For this reason, the measured value of α_2^H for 2,6-*t*-Bu_2-4-MeC_6H_2OH by a variety of methods and with various strong HBAs such as MeCN, THF, DMSO, and pyridine is not a single number but varies from 0.18 to 0.29.[55] Making this phenolic compound a reasonable model for 2,4,6-*t*-$Bu_3C_6H_2OH$, and using α_2^H = 0.24, we can calculate from eq 22 that $\Delta_r H(t\text{-}Bu_3C_6H_2OH\text{- - -}C_6H_6)_{18}^{benzene} = -0.2$ kcal mol^{-1}. However, benzene(s) HBA π-electron system makes it a relatively bulky HBA and therefore the $\Delta_r H_{18}^{benzene}$ for *t*-$Bu_3C_6H_2OH$ may well be zero. Given these uncertainties, we arbitrarily assign a value midway between these limits viz., − 0.1 kcal mol^{-1}, and hence the BDE(*t*-$Bu_3C_6H_2O-H$)^{gas} = 80.1−0.1 = 80.0 kcal mol^{-1}. For phenol (α_2^H = 0.596) eq 22 predicts $\Delta_r H(C_6H_5OH\text{- - -}C_6H_6)_{18}^{benzene} = -1.2$ kcal mol^{-1} and hence the corrected REqEPR BDE(C_6H_5O-H)^{gas} = 87.2 + 0.1−1.2 = 86.1 ± 0.8 (1 M standard state) or 86.5 ± 0.8 kcal mol^{-1} (1 atm standard state).

TABLE 4: Reevaluated Experimental Gas-Phase O−H BDEs for Phenol in kcal mol^{-1} at 298 K

method	O−H BDE
anisole pyrolysis	87.0 ± 0.4
diphenyl ether pyrolysis	86.9 ± 0.6
photoacoustic calorimetry (PAC)	86.3 ±1.0 [a]
one electron reduction (*E*°/*pK*$_a$)	87.0 ± 0.3
radical equilibrium EPR (REqEPR)	86.5 ± 0.8 [a]
average	86.7 ± 0.7

[a] Converted to the standard concentration state of 1 atm, eq 17.

The REqEPR O−H BDEs for all phenols[7,45,46] require first a downward correction by −1.1 + 0.1 = −1.0 kcal mol^{-1} and second a correction (which was −1.2 kcal mol^{-1} for phenol) to allow for hydrogen bonding of phenols to benzenes. These corrections can be obtained by using the appropriate tabulated or separately measured α_2^H values[11,30] and eq 22. These corrections will be larger than −1.2 for phenols that are better HBDs than C_6H_5OH and smaller than −1.2 for phenols that are poorer HBD, the correction will drop to about zero for 2,6-*tert*-butyl-4-substituted-phenols.

Conclusion. Four very different liquid-phase experimental procedures, namely photoacoustic calorimetry (PAC) in various solvents, one-electron reduction/acidity ($E°/pK_a$) in water, one-electron oxidation/acidity (E_{ox}/pK_a) in DMSO, and radical equilibrium EPR (REqEPR) in benzene have been used to determine BDE(C_6H_5O-H)^{gas}. A careful reanalysis of these results, with as rigorous an exclusion of solvent effects as possible, reveals that three of these techniques (PAC, $E°/pK_a$ and REqEPR) yield BDE(C_6H_5O-H) that are in excellent agreement with the ones derived from gas-phase kinetics (vide supra), underscoring the validity of the empirical solvent model used, see Table 4. When combining all results (gas-phase and liquid-phase data), a mean experimental O−H BDE of 86.7 ± 0.7 kcal mol^{-1} is found. The fourth procedure (E_{ox}/pK_a) was too badly flawed to yield a usable BDE(C_6H_5O-H)^{gas}.

Computational Studies. Having established a highly reliable *experimental* value for BDE (C_6H_5O-H) using both gas-phase kinetic data and the results of three different types of measurement in the liquid phase, the ability of *theory* to arrive at the same O−H BDE was explored.

The numerous calculations of O−H BDE in phenol up to 1997 have been summarized by Borges dos Santos and Martinho Simoes.[56] More recently, 13 different computational strategies yielded BDE(C_6H_5O-H)s ranging from 81.7 to 100.3 kcal mol^{-1}.[57] Previous work by some of us using density functional theory (DFT) based methods gave values in the range 87.0 ± 0.3 or 87.9 ± 0.9 kcal mol^{-1}, depending on the level of theory at which the geometries were optimized and whether a (RO)-B3LYP/6-311+G(2d,2p) or (U)B3P86/6-311G(2d,2p) approach was employed to calculate single point energies .[58] We will not discuss this earlier work but will focus, instead, on results obtained using current "state-of-the-art" computational approaches.[59]

The very highest level of theory that could be used to study this problem with our computing facilities is CCSD(T)/aug-cc-pVTZ.[60] This gave[61] a rather discouraging 89.0 kcal mol^{-1} for the O−H BDE in phenol. Extrapolation with larger basis sets to obtain a CCSD(T) BDE closer to the basis set limit, as has been done for smaller molecules,[62] with calculations using the correlation consistent quadruple-ζ basis set, were beyond our capabilities.[63] A basis set extrapolation with the larger aug-cc-pVQZ basis sets was possible but only with MP2, a level of

TABLE 5: Computed and Experimental BDEs in kcal mol^{-1} at 298 K and 1 atm[a]

	G3	CBS-APNO	CBS-QB3	BDE$_{exp}$[b]
CH_3O-H	105.1 (+0.5)	105.3 (+0.7)	105.3 (+0.7)	104.6 ± 0.7
CH_3O-CH_3	83.3 (+0.1)	84.6 (+1.4)	85.2 (+2.0)	83.2 ± 0.9 [c]
C_6H_5O-H	88.2 (+1.5)	88.2 (+1.5)	87.1 (+0.4)	**86.7** ± 0.7
$C_6H_5O-CH_3$	65.4 (0.1)	66.4 (+1.1)	65.7 (+0.4)	65.3 ± 0.4
CH_3-H	104.3 (−0.7)	105.4 (+0.4)	105.4 (+0.4)	105.0 ± 0.1
CH_3CH_2-H	101.2 (+0.1)	101.8 (+0.7)	101.7 (+0.6)	101.1 ± 0.4
$CH_3CH_2-CH_3$	88.0 (−1.0)	89.7 (+0.7)	89.7 (+0.7)	89.0 ± 0.4
$C_6H_5CH_2-H$	90.5 (+0.7)	91.4 (+1.6)	90.6 (+0.8)	89.8 ± 0.6
$C_6H_5CH_2-CH_3$	76.8 (−0.8)	78.6 (+1.0)	78.9 (+1.3)	77.6 ± 0.6

[a] In parentheses: BDE$_{calc}$ − BDE$_{exp}$. [b] From ref 2, except the gas-phase O−C BDE in anisole and the O−H BDE in phenol (this study). [c] The O−C BDE in CH_3OCH_3 resides on the O−H BDE in CH_3OH, the C−H BDE in CH_4, and the Δ_fH for CH_4, CH_3OH, CH_3OCH_3, and $H^{\bullet}$, which explains the large error of 0.9 kcal mol^{-1}.

TABLE 6: BDEs in C_6H_5Z-$H(CH_3)$ (Z = O, CH_2) in kcal mol^{-1} at 298 K and 1 atm According to Isodesmic Reactions 30 and 31

	G3	CBS-APNO	CBS-QB3	BDE$_{exp}$[b]
C_6H_5O-H	87.7 (+0.8)	87.5 (+0.8)	86.4 (−0.3)	86.7 ± 0.7
$C_6H_5O-CH_3$	65.3 (−0.1)	65.0 (−0.4)	63.7 (−1.7)	65.4 ± 0.3
$C_6H_5CH_2-H$	90.4 (+0.6)	90.7 (+0.9)	90.0 (+0.2)	89.8 ± 0.6
$C_6H_5CH_2-CH_3$	77.8 (+0.2)	77.9 (+0.3)	78.2 (+0.6)	77.6 ± 0.6

[a] In parentheses: BDE$_{comp}$ − BDE$_{exp}$. [b] From ref 2, except for the O−C BDE in anisole and the O−H BDE in phenol (this study).

theory that produces wave functions for the phenoxyl radical that are highly spin-contaminated and unreliable. Therefore, we turned to the calculation of heats of formation using Gaussian-3 (G3)[65] and two Complete Basis Set (CBS-APNO[66] and CBS-QB3[67]) methods which use a combination of techniques and corrections to obtain energies that approximate the fully correlated values.[68] The abilities of these three methods to yield BDEs close to the best experimental values were further explored with calculations on a number of other compounds, see Table 5.[69] It is clear that the two CBS methods overestimate each BDE in this test set, whereas G3 overestimates some and underestimates others, thus giving a better "average" performance. However, for the BDE of present interest, G3 gives a 1.5 kcal mol^{-1} overestimate as does CBS-APNO, whereas CBS-QB3 gives a value within the error limits of our reevaluated phenol O−H BDE.

The isodesmic reactions 30 and 31 (Z = O, CH_2) were also used in an effort to reduce inherent deficiencies in the computational methods and in order to calculate BDEs relative to (presumably) more accurate values.[70] The BDEs obtained in this way are given in Table 6.

$$C_6H_5Z^{\bullet} + CH_3ZH \rightarrow C_6H_5ZH + CH_3Z^{\bullet} \qquad (30)$$

$$C_6H_5Z^{\bullet} + CH_3ZCH_3 \rightarrow C_6H_5ZCH_3 + CH_3Z^{\bullet} \qquad (31)$$

With one exception ($C_6H_5O-CH_3$, CBS-QB3) they are in better agreement with the experiment than the values given in Table 5. Indeed, all three of these compound methods with isodesmic corrections give phenol O−H BDEs that are in good agreement with experiment considering the error limits we have assigned to the experimental value.

General Conclusion

This study has compiled and re-analyzed the available thermochemical data necessary to derive the O−H BDE in phenol. For the gas-phase, the thermal decomposition of anisole or diphenyl ether yield a BDE(C_6H_5O-H) of 87.0 ± 0.5 kcal mol^{-1}; the gas-phase ion cycle methodology is hampered by large errors. After careful elimination of the enthalpic effect of solvation (i.e., hydrogen bonding), three out of four liquid-phase experimental methods have yielded an O−H BDE(C_6H_5O-H) of 86.6 ± 0.7 kcal mol^{-1}, where the error margin includes all known experimental plus possible auxiliary errors. An empirical model is presented in this paper, which can adequately quantify solvent effects for the phenol/phenoxyl couple in water and other solvents. Based on these experimental data, we can conclude that the recommended gas-phase O−H BDE for phenol is 86.7 ± 0.7 kcal mol^{-1} at 1 atm standard state. This value deviates significantly from the one tabulated recently as 90 ± 3 kcal mol^{-1}.[2] The O−H BDEs from our computational efforts are fully commensurate with the new recommended value.

Acknowledgment. D.A.P. thanks Dr. Jarrod Smith and the Center for Structural Biology at Vanderbilt University for generous access to their computing facilities. H.G.K. thanks the Hochschulrechenzentrum Essen for the generous allotment of computer resources. The authors thank Dr. Grzegorz Litwinienko for the measurement of the hydrogen bond basicity of di-*tert*-butyl peroxide. L.V. and G.F.P. thank the University of Bologna and MIUR (research project "Free Radical Processes in Chemistry and Biology: Fundamental Aspects and Applications in Environment and Material Sciences") for financial support.

Supporting Information Available: Auxiliary experimental and G3 and CBS computed enthalpic data (Table S1), CBS-QB3 energies for the gas-phase ion cycles (Table S2); Appendix on the heat of formation of anisole; Hydrogen bonding in binary solvent systems (Tables S3 and S4); Computational solvent models (Table S5). This material is available free of charge via Internet at http://pubs.acs.org.

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