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Effects of Solvation on the Enthalpies of Reaction of *tert*-Butoxyl Radicals with Phenol and on the Calculated O−H Bond Strength in Phenol[1]

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Abstract: The enthalpy for the reaction of di-*tert*-butyl peroxide with phenol to give *tert*-butyl alcohol and phenoxyl radical (i.e. t-BuOOBu-t + 2 PhOH → 2 t-BuOH + 2 PhO$^\bullet$) has been determined in a number of solvents using photoacoustic calorimetry. The effect of the solvent on the thermochemistry of this process is remarkably large with the reaction being ca. 10 kcal mol^{-1} more exothermic in acetonitrile or ethyl acetate than in isooctane. The relationship between the observed enthalpy changes and the PhO−H bond energy is discussed in detail. It is shown that in order to extract the bond energy from the experimental (apparent) enthalpy change, it is necessary to account for a number of processes, viz., the volume change for the overall reaction, the solvent effect associated with the conversion of 1 mol of di-*tert*-butyl peroxide to 2 mol of *tert*-butyl alcohol, and the differences in solvation of phenol and the phenoxyl radical. The contributions from each of these processes to the observed reaction enthalpy were derived from a separate set of experiments with 1,4-cyclohexadiene instead of phenol or from data available in the literature. These data allow one to determine solution bond energies, i.e., the enthalpy of homolysis for which the standard state is the solvated reactant and products, and to quantify the solvent effect on these values. Thus, PhO−H bond energies in isooctane (88 kcal mol^{-1}), benzene (89 kcal mol^{-1}), carbon tetrachloride (90 kcal mol^{-1}), ethyl acetate (95 kcal mol^{-1}), and acetonitrile (95 kcal mol^{-1}) have been obtained. Most of the differences between these values can be accounted for from the known hydrogen bonding equilibrium between the solvents and the phenol. A number of purported determinations of the PhO−H "gas-phase bond energy" which utilized electrochemical (EC) measurements and, of necessity, highly polar solvents are shown to be seriously in error. Similar errors must be present in many other EC "gas-phase" bond energies which also were determined in polar solvents.

Bond dissociation energies (BDE) are of fundamental importance because they permit chemists to decide whether or not a particular reaction will be enthalpically favored. Such decisions are usually based on bond dissociation energy differences (ΔBDEs). For example, for the hydrogen atom abstraction

$$X^\bullet + RH \rightarrow XH + R^\bullet \qquad (1)$$

the reaction enthalpy, ΔH_r, is determined from the difference in BDEs for XH (eq 2) and RH (eq 3), ΔBDE = BDE(X−H) − BDE(R−H). Unfortunately, the vast majority of BDEs in the

$$XH \rightarrow X^\bullet + H^\bullet \qquad (2)$$

$$RH \rightarrow R^\bullet + H^\bullet \qquad (3)$$

literature refer to gas-phase reactions, while most of the chemistry to which they are applied occurs in solution. However, even for homolytic reactions involving a neutral radical and substrate, it is not certain that the quantity $(\Delta BDE)^{gas}$ will be equal to $(\Delta BDE)^{sol}$. In addition, many BDEs of interest to organic chemists have not been measured in the gas phase and, at least partly for this reason, a variety of techniques have been developed which purport to measure BDEs in solution.

Photoacoustic calorimetry (PAC),[2] electrochemical (EC)[3−6] and other[7] measurements have been used to determine the O−H BDE of phenol in solution, BDE(PhO−H)^{sol}. However, the results obtained cover a range of nearly 8 kcal mol^{-1} (from 84 to 91.6 kcal mol^{-1}, see Table 1) and they bracket the estimated gas-phase BDE values[8−11] which range from 85.1 to 88.3 kcal mol^{-1}, with a best value estimated to be ca. 87 kcal mol^{-1}.[8−11] The range of the solution values for BDE(PhO−H)^{sol} is well

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Table 1. Values of BDE(O−H) of Phenol from the Recent Literature

solvent	method	BDE(O−H), kcal mol^{-1}	ref
benzene	PAC	84.0	2
water	EC	88.2[a]	4
dimethyl sulfoxide	EC	89.9	5
b	EC	91.6	6
chlorobenzene	*c*	88.3	7
none[d]	*e*	85.1[f]	2
none[d]	*e*	86.5	8
none[d]	*g*	86.8	9
none[d]	*h*	88.3	10
none[d]	*i*	87.2	11
none (recommended value)		ca. 87	

[a] Upper limit, see also ref 3. [b] BDE(O−H) calculated from pK_a measured in DMSO and E_{ox} measured in sulfolane. [c] Kinetic method based on a computer fit to experimental data for the ROO$^\bullet$ + PhOH $\rightleftarrows$ ROOH + PhO$^\bullet$ reaction and a measured value for BDE(ROO−H)$_{sol}$. [d] Gas phase. [e] Rates of thermolysis of phenyl allyl ether and phenyl ethyl ether, ref 8. [f] Data from ref 8 have been corrected to reflect more recent measurements of the heats of formation of reactants and products (see footnote 21 in ref 2). [g] Measurement of the enthalpy of formation of PhO$^\bullet$ by ion cyclotron double resonance. [h] Rates of thermolysis of *n*-butyl phenyl ether. [i] Rates of thermolysis of anisole.

outside the claimed experimental errors (which are generally ca. ±2 kcal mol^{-1}).

It should be noted that neither the EC technique nor the PAC technique for measuring BDEs is a stand-alone method. Both techniques are dependent upon at least one gas-phase measurement. The EC technique,[12] as developed by Bordwell and his co-workers,[5] makes use of literature gas-phase BDE's and then measures differences in BDEs, ΔBDE, between this bond, now in solution, and the same bond in a series of related molecules in the same solvent with the implicit assumption that there is no solvent effect on the BDEs. In fact, the EC technique actually measures the free-energy differences ($\Delta\Delta G^\circ_{BDE}$) for cleavage of the reference and unknown bond and it is then assumed that ΔS° is the same for all the bond cleavage reactions studied, i.e., $\Delta\Delta S^\circ = 0$, and, moreover, that ΔS° for the reference BDE is the same in solution as in the gas phase. All of these assumptions are contained in an empirical constant in a deceptively simple equation that relates the BDE(X−H) to the pK_a(X−H) and the standard potential of the conjugate base, E°(X$^\bullet$/X$^-$). On the other hand, in the PAC technique the enthalpy change for a photoinduced reaction is measured and then (using an equally deceptively simple equation) relies on gas-phase heats of formation of some of the reactants and products to extract the desired BDE (*vide infra*).

In the present paper, we show that the magnitude of BDE(PhO−H)^{sol} measured by the PAC technique is dependent on the solvent in which the measurement has been made. Furthermore, we demonstrate that the variation in the magnitude of BDE(PhO−H)^{sol} between different solvents is due to differences in the heats of solvation of the reactants and products in the different solvents. The problems associated with the measurement of BDE(PhO−H)^{sol} by the PAC and EC techniques are examined and the sources of error are analyzed.

Results

The PAC Technique. This involves measurement of the heat released when a brief pulse of radiation from a laser strikes a solution containing the reactants and initiates a predetermined chemical change. The energy released generates an acoustic shock wave which is recorded by a sensitive microphone attached to the reaction vessel. The PAC technique actually involves the measurement of a laser pulse-induced volume change which can be converted to an enthalpic change, ΔH_{obs}, provided the thermoelastic properties of the solvent are known (i.e., the heat capacity, C_p°, and the thermal expansion coefficient, β). This is a comparative method in which a known amount of energy absorbed by the system induces a chemical transformation with the residual energy being returned to the system as heat. The volume change that is actually measured consists of two components: that which is due to the thermal expansion and that which is due to a volume change on going from reactants to products. The former is the quantity required for bond energy determinations. The latter is generally significant only when the number of chemical species changes, i.e., when the number of bonds broken is not the same as the number of bonds formed.

Although this subject has been discussed in detail elsewhere,[14] it is useful to review briefly the origin of the photoacoustic signal. The magnitude of the observed acoustic signal, S_{obs}, is most simply expressed by eq 4 in which f_{obs} is the *apparent* fraction of photon energy released as heat (see below), $E_{h\nu}$ is the photon energy, OD is the optical density at the laser wavelength, and χ_s is the adiabatic expansion coefficient of the solvent for which the parameters (β, the thermal expansion coefficient; MWt, the molecular weight of the solvent; ϱ, the density; and C_p°, the heat capacity) are given in eq 5. The constant c is determined by the geometry of the cell and a number of other instrument parameters. The observed volume change can be expressed as eq 6 where f_{th} is the fraction of the photon energy actually converted into heat and ΔV_{chem} is the volume change associated with the overall reaction.

$$S_{obs} = cf_{obs}E_{h\nu}(1 - 10^{-OD})\chi_s \tag{4}$$

$$\chi_s = \frac{\beta MWt}{\varrho C_p^\circ} \tag{5}$$

$$f_{obs}E_{h\nu}\chi_s = f_{th}E_{h\nu}\chi_s + \Delta V_{chem} \tag{6}$$

The relationship between f_{th} and the reaction enthalpy, ΔH_r, is given by eq 7, while that for the volume of reaction, ΔV_r, is given by eq 8. In both cases, the observed values must be corrected for the photochemical quantum yield of the reaction studied, Φ, since not every absorbed photon will lead to product formation.[14]

$$\Delta H_r = \frac{E_{h\nu}}{\Phi}(1 - f_{th}) \tag{7}$$

$$\Delta V_r = \frac{\Delta V_{chem}}{\Phi} \tag{8}$$

Determination of BDE(PhO−H)^{sol} by PAC involves the irradiation of a solution containing phenol and di-*tert*-butyl peroxide with pulses from a nitrogen laser (337 nm, pulse width either 0.6 or 8 ns, up to 50 μJ/pulse). This instantaneously produces *tert*-butoxyl radicals, eq 9, which subsequently abstract phenolic hydrogen atoms from the phenol, eq 10. The kinetic requirement is that reaction 10 be complete in less than 100 ns so that heat is evolved on a time scale which is much faster than the intrinsic response of the microphone (ca. 2 μs). This is achieved by ensuring that the phenol concentration is such

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(12) The use of thermochemical cycles to predict gas-phase properties from liquid-state measurements or vice versa was pioneered by Eberson.[13]

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that k_{10}[PhOH] ≥ 1 × 10^7 s^{-1}.

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuCO}^\bullet \qquad (9)$$

$$t\text{-BuO}^\bullet + \text{PhOH} \xrightarrow{k_{10}} t\text{-BuOH} + \text{PhO}^\bullet \qquad (10)$$

Since the magnitude of k_{10} depends on the solvent[15,16] it is good practice to measure the lifetime, $\tau = (k_{10}[\text{PhOH}])^{-1}$, for the grow-in of the phenoxyl radical following the laser pulse using a kinetic laser flash photolysis (LFP) system prior to any PAC experiments. The grow-in of the phenoxyl radical can be monitored via its absorption at 400 nm. The phenol concentration is then adjusted until $\tau \leq 100$ ns and thus the conditions suitable for a PAC experiment are defined for each solvent.

If the kinetic criterion is met, the intermediate *tert*-butoxyl radical is short-lived compared to the response time of the microphone and the observed acoustic signal will contain information related to ΔH_r and ΔV_r for the *overall* reaction shown in eq 11. These signals contain contributions from the energy of the laser pulse (337 nm ≡ 84.8 kcal/mol), the enthalpy for the endothermic O—O bond cleavage (eq 9), and the enthalpy for the exothermic hydrogen atom abstraction (eq 10).

$$t\text{-BuOOBu-}t + 2\text{PhOH} \rightarrow 2t\text{-BuOH} + 2\text{PhO}^\bullet \qquad (11)$$

For reactions 9 and 10 there are solvent-dependent contributions to S_{obs} which must be taken into account. For reaction 9 these are the following: (i) the quantum yield, Φ_9, for the formation of freely diffusing pairs of *tert*-butoxyl radicals, (ii) a contribution to the photoacoustic signal from the change in volume upon going from reactants to products, ΔV_9, and (iii) differences in the enthalpies of solvation of the reactants and products. For reaction 10, only item (iii) in the above list is of concern since ΔV_r for a metathesis reaction will be negligible. Each of these concerns about solvent-dependent quantities will be addressed after the following brief description of the general experimental procedure.

A relative experimental method is employed in which the photoacoustic signal generated in the reaction vessel, S_{obs}, is recorded as a function of the number of 337-nm photons absorbed by the sample ($1-10^{-\text{OD}}$). This signal is normalized, in order to allow for variations in photon flux, by dividing by the average laser energy which is monitored simultaneously. The magnitude of $1 - 10^{-\text{OD}}$ is altered by carrying out experiments using different concentrations of peroxide. A plot of S_{obs} vs $1 - 10^{-\text{OD}}$ then yields an excellent straight line ($r \geq 0.9996$) with a slope a_{obs}. Under the same experimental conditions the microphone response is calibrated using a reference compound which absorbs at 337 nm and converts all the absorbed energy to heat. Suitable compounds are *o*-hydroxybenzophenone and ferrocene.[14] A plot of these photoacoustic signals from the reference S_{ref} vs $1 - 10^{-\text{OD}}$ yields a second linear correlation with a slope a_{ref}. The apparent fraction of photon energy converted to heat, f_{obs}, which is required (eq 6) is given by eq 12.

$$f_{\text{obs}} = a_{\text{obs}}/a_{\text{ref}} \qquad (12)$$

Measurement of the Quantum Yield, Φ_9, for the Photolysis of Di-*tert*-butyl Peroxide. The absolute magnitude of Φ_9 in different solvents can best be determined by actinometry but, to our knowledge, this method has not previously been employed for this reaction. Two PAC measurements of Φ_9 in carbon tetrachloride[17] and benzene[18] have been reported but volume corrections (*vide supra* and *infra*) were not considered, resulting in considerable errors. More interestingly, Kiefer and Traylor[19] used the relative rates of photodecomposition of di-*tert*-butyl peroxide in a number of *n*-alkane solvents to estimate relative quantum yields. These were converted to absolute quantum yields by assuming a cage effect of 4% in *n*-pentane, i.e., $(\Phi_9)_{\text{pentane}} = 0.96$. However, in these experiments the broad unfiltered UV emission from a high-pressure Xe/Hg lamp was employed and, apparently, it was assumed that the molar extinction coefficients of the peroxide were solvent independent.[20]

In order to obtain quantum yield data that are pertinent to the exact conditions used in the PAC experiments (and which overcome deficiencies in the earlier measurements) we developed a procedure which employed the same pulsed nitrogen laser as was used in the PAC experiments (see Experimental Section). This made it relatively simple to match the 337 nm optical densities in the different solvents.

In these experiments, pulsed (10 Hz) laser irradiations were carried out for well-defined lengths of time. Aberchrome 540 and azoxybenzene (2—4 mM) were employed as actinometers. The quantity of di-*tert*-butyl peroxide decomposed was determined by measuring the absolute yields of *tert*-butyl alcohol which were produced. For hydrocarbon solvents the hydrogen atom source was the solvent itself. Under these conditions the pseudo-first-order lifetime of the *tert*-butoxyl radical will be ca. 200 ns and, therefore, essentially all the radicals which escape from the solvent cage in which they were formed will be converted into *tert*-butyl alcohol. For benzene as solvent, tris(trimethylsilyl)silane or triethylamine served as the hydrogen atom source. They were used at concentrations of 0.05 M which would again give the *tert*-butoxyl radical a lifetime of ca. 200 ns. Since the conversion of di-*tert*-butyl peroxide in these experiments was very low, concentrations of *tert*-butyl alcohol were determined relative to two internal GC standards (benzene and chlorobenzene or benzonitrile and chlorobenzene) which were added to the solution of the peroxide (0.5—0.7 mM) prior to irradiation. Plots of [*tert*-butyl alcohol] vs duration of irradiation were linear provided <2% of the peroxide was consumed. After each period of irradiation (and measurement of [*tert*-butyl alcohol]) the number of photons absorbed was determined by subjecting a matched (OD at 337 nm) solution of the actinometer to the laser pulses for between 3 and 5 min. Plots of OD_{494} (Aberchrome 540) or OD_{458} (azoxybenzene) vs irradiation time also were linear for the duration of these experiments. The slopes of the straight lines in these plots, R_{act}, are related to the number of quanta delivered per second, Q, by eq 13:

$$Q = \frac{R_{\text{act}}}{\epsilon_{\text{act}}(\Phi_{337})_{\text{act}}} \qquad (13)$$

Photophysical data for the two actinometers are available, viz., for Aberchrome 540, $\epsilon_{494} = 8200\ \text{M}^{-1}\ \text{cm}^{-1}$, $\Phi_{337} = 0.2$

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(19) Kiefer, H.; Traylor, T. G. *J. Am. Chem. Soc.* **1967**, *89*, 6667–6671.

(20) It would appear that Kiefer and Traylor[19] used low concentrations of peroxide but there is no indication as to whether or not the optical absorptions of each sample were matched with respect to overlap with the spectral output of the lamp.

Table 2. Quantum Yield (Φ_9) for Photolysis of Di-*tert*-butyl Peroxide

solvent	Φ_9[a]	χ_s, mL kcal^{-1} [b]
hexane	0.93	3.84
acetonitrile	0.89	3.35
ethyl acetate	0.86[c]	3.27
heptane	0.85	3.32
isooctane	0.84[c]	3.45
benzene	0.83	3.30
nonane	0.81	2.81
carbon tetrachloride	0.76[c]	3.70
hexadecane	0.68	2.18

[a] Measured by actinometry (see Experimental Section) unless otherwise noted. These values have a relative error of ±0.03. [b] Data used to calculate χ_s from: Marcus, Y. *Ion Solvation*; Wiley: New York, 1985, Chapter 6. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; Wiley: New York, 1980. [c] Interpolated using Figure 1 and the solvent's viscosity.

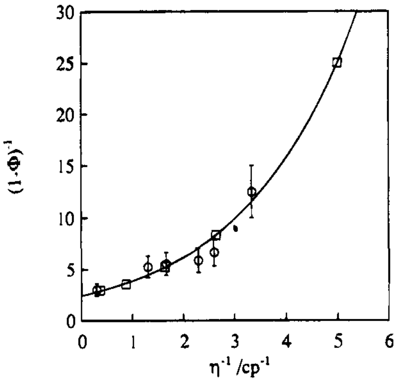


Figure 1. Plot of $(1 - \Phi)^{-1}$ versus η^{-1} for the photodecomposition of di-*tert*-butyl peroxide in a number of hydrocarbon solvents; ○, this work; □, data from ref 19.

in toluene,[21] and for azoxybenzene, ϵ_{458} = 7600 M^{-1} cm^{-1}, Φ_{337} = 0.025 in ethanol.[22] The quantum yields for the 337-nm photolyses of di-*tert*-butyl peroxide, Φ_9, were calculated from eq 14 where the factor of 0.5 takes account of the stoichiometry of the overall process. The results are given in Table 2.

$$\Phi_9 = \frac{0.5\,\dfrac{d[t\text{-BuOH}]}{dt}}{Q} \qquad (14)$$

The fraction of geminate *tert*-butoxyl radical pairs that undergo collapse within the solvent cage to reform di-*tert*-butyl peroxide, i.e., $1 - \Phi_9$, is both expected and found to decrease as the solvent viscosity, η, decreases. In fact, our data and the data of Kiefer and Traylor[19] are in remarkably good agreement as can be seen in Figure 1 which shows the usual[23] plot of $(1 - \Phi_9)^{-1}$ vs η^{-1}. Consequently, the values of Φ_9 in those solvents for which it was not measured experimentally were estimated from the solvent's viscosity using this plot. It is interesting to note that this double reciprocal plot shows the upward curvature in low-viscosity solvents as has been observed by others.[19,23]

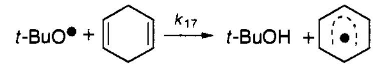
The Volume of Reaction Correction. The volume change for the overall process (eq 11) is expected to be dominated by the volume change due to the photocleavage of di-*tert*-butyl peroxide (eq 9). Based on volumes of activation, $\Delta V^{\ddagger}$, reported by Walling and Metzger,[24] the volume change for formation of two *tert*-butoxyl radicals from di-*tert*-butyl peroxide is expected to be ca. 13 mL mol^{-1}. This value is in qualitative agreement with the suggestion of le Noble and Kelm[25] that activation volumes should be roughly 10 mL mol^{-1} per bond broken. Volume changes, ΔV_r, of similar magnitude (per bond) have been reported by Hung and Grabowski.[26] Since the di-*tert*-butyl peroxide bond dissociation enthalpy in solution can be reasonably expected to be about the same as in the gas phase (ΔH_9 = 38 kcal mol^{-1}),[27] it is possible to estimate the volume change involved in reaction 9. The most straightforward approach is to compare the apparent quantum yield, Φ_{app} (eq 15), for the photolysis of di-*tert*-butyl peroxide in the absence of a hydrogen atom donor to that determined by actinometry (Φ_9, Table 2). Two suitably inert solvents are benzene and carbon tetrachloride.[28] By manipulation of eqs 6–8 and 15, ΔV_r can be determined (eq 16).

$$(\Phi_9)_{app} = \frac{84.8}{\Delta H_9}(1 - f_{obs}) \qquad (15)$$

$$\Delta V_r = \left(1 - \frac{(\Phi_9)_{app}}{\Phi_9}\right)\chi_s \Delta H_9 \text{ mL mol}^{-1} \qquad (16)$$

For benzene and carbon tetrachloride the values of $(\Phi_9)_{app}$ (0.75 and 0.68, respectively) and Φ_9 (0.83 and 0.76, respectively, see Table 2) lead to values of ΔV_r of 12.1 and 14.8 mol^{-1}, respectively (mean = 13.4 ± 4 mL mol^{-1}), that are, as expected, independent of solvent. These values also correspond rather well with the values of $\Delta V^{\ddagger}$ reported by Walling and Metzger[24] of 12.6 and 13.3 mL mol^{-1} in benzene and carbon tetrachloride, respectively (mean = 13.0 mL mol^{-1}). Again, this is not surprising since the O–O bond is essentially broken at the transition state.

Measurement of Differences in the Enthalpies of Solvation of the Reactants and Products. On the PAC time scale reactions 9 and 10 can be considered as a single process insofar as differences in the solvation enthalpies of reactants and products are concerned (eq 11). Both PhOH and *t*-BuOH will form hydrogen-bonded complexes with H-bond accepting solvents, i.e., with Lewis base solvents (which include benzene), and the enthalpies for formation of such complexes certainly will not be identical for PhOH and *t*-BuOH. In addition, all of the reactants and products might, in principle, interact with polar and polarizable solvents in other ways (e.g., via dipole–dipole or dipole–induced dipole forces). In order to simplify the problem of solvation enthalpies posed by reaction 11 we decided to apply the PAC technique to a simpler system in which only a single hydrogen bond donor would be involved, *t*-BuOH. As the substrate we chose 1,4-cyclohexadiene (eq 17) because this hydrocarbon is known to react rapidly with *t*-BuO$^{\bullet}$ radicals.[29]



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[28] Although isooctane can be used as a solvent for bond energy determinations, the lifetime of the *tert*-butoxyl radical in the neat solvent is ca. 1 μs. Thus, an additional contribution to the photoacoustic signal from hydrogen atom abstraction in the determination of Φ_{app} is expected.

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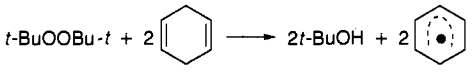
Table 3. Apparent Enthalpies of Reaction for Eq 18 Determined by PAC[a]

solvent	$(\Delta H_{18}^{sol})_{app}$, kcal mol^{-1}	$(\Delta\Delta H_{solv})_{app}$[b], kcal mol^{-1}	$\Delta V_r/\chi_s$,[c] kcal mol^{-1}
isooctane	−30	−10	3.9
carbon tetrachloride	−29	−9	3.6
benzene	−29	−9	4.1
acetonitrile	−33	−13	4.0
ethyl acetate	−33	−13	4.1

[a] Average of at least four independent determinations. The experimental error is ±2 kcal mol^{-1}. [b] In the gas phase the bond dissociation energy of 1,4-cyclohexadiene is 76 kcal mol^{-1} (Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152–1155) leading to $\Delta H_{18}^{gas} = -20.3$ kcal mol^{-1}. [c] Assuming an average value of $\Delta V_r = 12.3$ mL mol^{-1} (see text and Table 2).

In previous work we demonstrated that the rate constant for hydrogen atom abstraction from cyclohexane is independent of the solvent[30] (in contrast to hydrogen abstraction from phenol, k_{10}[15,16]). As would be expected, a kinetic LFP study showed that the rate of reaction 17 was also solvent independent: $k_{17} = 3.0 \pm 0.4 \times 10^7$ M^{-1} s^{-1} in isooctane, carbon tetrachloride, benzene, and acetonitrile at 20 °C. With such a high rate constant the lifetime of the t-BuO$^•$ radicals will be <100 ns at 1,4-cyclohexadiene concentrations of ca. 0.5 M in all of these solvents which makes PAC experiments practicable.

Cyclohexadiene will have no dipole moment and the cyclohexadienyl radical can have only a very small dipole moment. We can therefore safely assume that the enthalpies of solvation of this hydrocarbon and its radical will be essentially equal in any particular solvent.[31] Thus, a PAC study of the overall reaction (eq 18), permits the assessment of the change in the heats of solvation, $\Delta\Delta H_{solv}$, for a process which converts one di-*tert*-butyl peroxide into two *tert*-butyl alcohols. That is, after correction for ΔV_r, the PAC experiment will yield ΔH_{18}^{sol}. The difference between the gas-phase value, ΔH_{18}^{gas}, and this value is given by eqs 19 and 20.



(18)

$$\Delta\Delta H_{solv} = \Delta H_{18}^{sol} - \Delta H_{18}^{gas} \qquad (19)$$

$$\Delta\Delta H_{solv} = 2\Delta H_{solv}(t\text{-BuOH}) - \Delta H_{solv}(t\text{-BuOOBu-}t) \qquad (20)$$

It is not necessary to correct explicitly for ΔV_r. By using the apparent enthalpy change, $(\Delta H_{18}^{sol})_{app}$ (i.e., using f_{obs} rather than f_{th}), eqs 19 and 20 will then include the volume correction to the enthalpy change as shown in eq 21.

$$(\Delta\Delta H_{solv})_{app} = (2\Delta H_{solv}(t\text{-BuOH}) - \Delta H_{solv}(t\text{-BuOOBu-}t)) - \frac{\Delta V_r}{\chi_s} \qquad (21)$$

The magnitude of $(\Delta\Delta H_{solv})_{app}$ provides an intersolvent correction factor which should be applied whenever di-*tert*-butyl peroxide is used as a reactant and the PAC technique is applied to other hydrogen atom donor substrates, including phenol. In principle, either eq 20 or 21 can be used to correct the observed enthalpy changes; eq 21 has the advantage of not requiring a prior estimate of the ΔV_r since this term is included implicitly in the correction. Experimentally derived values of $(\Delta H_{18}^{sol})_{app}$ for 1,4-cyclohexadiene are summarized in Table 3. With the assumption that the BDE for 1,4-cyclohexadiene is the same in solution as in the gas phase, the correction factor $(\Delta\Delta H_{solv})_{app}$ (= $(\Delta H_{18}^{sol})_{app} - \Delta H_{18}^{gas}$) is typically ca. −11 kcal mol^{-1} (see Table 3).

Calculation of (BDE)^{sol} from a PAC Experiment. In a particular solvent, A, we have, for the generalized reaction shown in eq 22, an apparent enthalpy change, $(\Delta H_{22}^{A})_{app}$, which is defined by eq 23.

$$t\text{-BuOOBu-}t + 2RH \rightarrow 2t\text{-BuOH} + 2R^• \qquad (22)$$

$$(\Delta H_{22}^{A})_{app} = \frac{84.8}{\Phi_9^{A}}(1 - f_{obs}) \quad (\text{kcal mol}^{-1}) \qquad (23)$$

The enthalpy balance for reaction 22 is given by eq 24a (where the superscript refers to the solvent) or, alternatively, as eq 24b in which some gas-phase enthalpies of formation, $\Delta H_f°$, are incorporated.

$$(\Delta H_{22}^{A})_{app} = 2\Delta H_f^A(R^•) + 2\Delta H_f^A(t\text{-BuOH}) - 2\Delta H_f^A(RH) - \Delta H_f^A(t\text{-BuOOBu-}t) - \frac{\Delta V_r}{\chi_s} \qquad (24a)$$

$$(\Delta H_{22}^{A})_{app} = 2\Delta H_f^A(R^•) + 2\Delta H_f^\circ(t\text{-BuOH}) - 2\Delta H_f^A(RH) - \Delta H_f^\circ(t\text{-BuOOBu-}t) + (\Delta\Delta H_{solv})_{app} \qquad (24b)$$

Since the BDE(R−H) in the gas phase is defined by eq 25a, the BDE(R−H) *in solution* obtained from the PAC experiment is defined by eq 25b and can, after manipulation of eqs 24b and 25a, be written as eq 26. In this equation, the constant 86.1

$$\text{BDE(R−H)}^{gas} = \Delta H_f^\circ(R^•) + \Delta H_f^\circ(H^•) - \Delta H_f^\circ(RH) \qquad (25a)$$

$$\text{BDE(R−H)}^{A} = \Delta H_f^A(R^•) + \Delta H_f^A(H^•) - \Delta H_f^A(RH) \qquad (25b)$$

$$\text{BDE(R−H)}^{A} = \frac{(\Delta H_{22}^{A})_{app}}{2} - \frac{(\Delta\Delta H_{solv})_{app}}{2} + \Delta H_{solv}^{A}(H^•) + 86.1 \qquad (26)$$

comes from the relevant gas-phase heats of formation (in kcal mol^{-1} at 298 K) $\Delta H_f^\circ(t\text{-BuOH}) = -74.7$,[33] $\Delta H_f^\circ(H^•) = 52.1$,[33] and $\Delta H_f^\circ(t\text{-BuOOBu-}t) = -81.2$[27] and $\Delta H_{sol}^{A}(H^•)$ is the enthalpy of solvation of the hydrogen atom which is relatively constant in isooctane, benzene, chlorobenzene, acetonitrile, dimethyl sulfoxide, and *N,N*-dimethylformamide with an average value of 2 ± 0.5 kcal mol^{-1}.[3]

Solvent Effects on the BDE(O−H) of Phenol. Using eq 26, we have determined BDE(O−H)^{sol} of phenol in isooctane, benzene, carbon tetrachloride, acetonitrile, and ethyl acetate. These data are given in Table 4.

Discussion

Many of the problems and difficulties involved in making reliable PAC measurements of the BDE(O−H)^{sol} of phenol were described in the Results section. Nevertheless, before considering the BDE(O−H)^{sol} values listed in Table 4 it is worth considering the error limits which should be placed upon these values and the origin of these errors. By far the largest source of error arises in attempting to determine the precise magnitude of the ratio of the slopes of the plots of the photoacoustic signal

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[30] Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466–470.

[31] It has been demonstrated that organic molecules, RH, and their corresponding radicals, R$^•$, are solvated to the same extent—even in water.[32]

[32] Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311–3314.

[33] NIST Standard Reference Data Base 25. *Structures and Properties Database and Estimation Program*, Version 2.01, 1994.

Table 4. Solution Bond Energies, BDE(O−H)^{sol} for Phenol[a,b]

solvent	$(\Delta H_{11}^{sol})_{app}$	BDE(O−H)^{sol}	ΔH_{28}^{A}(PhOH- - -A)[c]	BDE(O−H)^{gas} [d]
isooctane	−9.8	88.2	0[e]	86.2
carbon tetrachloride	−5.1	90.0	0[f]	88.0
benzene	−6.5	89.3	1.0[g]	86.3
acetonitrile	0.8	95.0	4.7[h]	88.3
ethyl acetate	0.7	95.0	4.7[i]	88.3
				av 87.4
gas phase				87[j]

[a] Using eq 26. [b] All values in kcal mol^{-1}. [c] Based on enthalpies of hydrogen bond formation between phenol and solvent A measured in CCl_4 unless otherwise noted. [d] Calculated by subtracting from BDE(O−H)^{sol} (column 3) 2.0 kcal mol^{-1} for the enthalpy of solvation of the hydrogen atom, $\Delta H_{solv}^{A}(H^{\bullet})$, and the appropriate enthalpy of hydrogen bond formation between phenol and the solvent, ΔH_{82}^{A}(PhOH- - -A) (column 4). [e] Assumed. [f] By definition. [g] An average value for ΔH_{sol}^{A}(PhOH- - -A) is 1.3 kcal mol^{-1} (refs 16 and 36a,b). However, at the concentration of PhOH used, the fraction complexed to the solvent is 0.8. Hence, a weighted average (0.8 × 1.3 = 1.0 kcal mol^{-1}) was used. [h] References 36c−f. [i] References 36b,e. [j] Recommended value, see text.

for the reaction, S_{obs}, and of the signal for the reference, S_{ref}, vs $1 - 10^{-OD}$ (eq 12). Although two exceptionally good straight lines are obtained ($r \geq 0.9996$ or the run is discarded from the overall data set), an error of 1−2% in the ratio of the slopes, $f_{obs} = a_{obs}/a_{ref}$ (eq 12), which is not at all unrealistic, would carry through to produce an error of ca. 0.8−1.5 kcal mol^{-1} in the calculated value for BDE(O−H)^{sol}. This experimental error is the single most important source of error in the PAC experiment.[34] Fortunately, the measured values of f_{obs} appear to be more reliable than ± 2% in each solvent as is indicated by the random errors for $(\Delta H_{18}^{sol})_{app}$ shown in Table 3, footnote *a*.

The BDE(O−H)^{sol} for phenol can now be calculated using the appropriate correction terms for the volume change and the differences in the heats of solvation between di-*tert*-butyl peroxide and *tert*-butyl alcohol. If we therefore assume that the errors in the BDE(O−H)^{sol} values are not greater than ±1.5 kcal mol^{-1} then the BDEs in Table 4 can be seen to fall into three groups: first, the gas-phase value of ca. 87 kcal mol^{-1}; second, those solvents which are not Lewis bases or are only poor Lewis bases, viz., isooctane, carbon tetrachloride, and benzene, with BDE(O−H)^{sol} in the range 88.2−90.0 kcal mol^{-1}; third, the two solvents which are strong Lewis bases and hence will act as strong hydrogen bond acceptors (HBA) to phenol, viz., acetonitrile and ethyl acetate, with BDE(O−H)^{sol} of 95.0 kcal mol^{-1}.

By definition, the relationship between BDE(O−H)^{gas} and BDE(O−H)^{sol} in solvent A simply requires subtraction from the latter of the enthalpy of solvation of the hydrogen atom[35] and the difference in the enthalpy of solvation of phenol and the phenoxyl radical, i.e.,

$$\mathrm{BDE(O{-}H)^{gas}} = \mathrm{BDE(O{-}H)^{A}} - \Delta H_{solv}^{A}(\mathrm{H}^{\bullet}) - (\Delta H_{solv}^{A}(\mathrm{PhO}^{\bullet}) - \Delta H_{solv}^{A}(\mathrm{PhOH})) \quad (27)$$

The major and possibly the only difference between ΔH_{solv}^{A}(PhOH) and $\Delta H_{solv}^{A}(PhO^{\bullet})$ will be due to hydrogen bond formation between the phenol and the solvent (eq 28) if the latter is a HBA solvent. This leads to a simple relationship between the bond energies in the gas phase and in solution (eq 29) where ΔH_{28}^{A}(PhOH- - -A) is the enthalpy of the hydrogen bond.

$$\mathrm{PhOH + A \rightleftharpoons PhOH{-}{-}{-}A} \quad (28)$$

$$\mathrm{BDE(O{-}H)^{gas}} = \mathrm{BDE(O{-}H)^{A}} - \Delta H_{solv}^{A}(\mathrm{H}^{\bullet}) - \Delta H_{28}^{A}(\mathrm{PhOH{-}{-}{-}A}) \quad (29)$$

There is a very extensive literature on the hydrogen-bonding equilibria (eq 28) between a wide variety of phenols and an even wider variety of HBA solvents.[36] In addition, there is very good evidence in the case of phenol itself[16,37] that each molecule of phenol can act as a hydrogen bond donor to only a single HBA molecule, A, at any one time. Furthermore, the available evidence suggests that the magnitude of the equilibrium constant, K_{28}^{A} for formation of each PhOH- - -A hydrogen-bonded complex, is essentially independent of the nature of the surrounding medium (e.g., the medium's dielectric constant).[16,37] Therefore, for our purposes it is immaterial whether the equilibrium constant or Van't Hoff parameters for eq 28 have been determined in the pure HBA solvent, A, or, as is more usual, in CCl_4 containing a small amount of A.[16,37]

With the foregoing ideas in mind and using literature data for the hydrogen bond enthalpies (see column 4 of Table 4) we are able to confirm (within our experimental accuracy) the validity of eq 29. For example, the PAC experiments in acetonitrile and ethyl acetate both yield BDE(O−H)^{sol} values of 95 ± 1 kcal mol^{-1}. After subtraction of the enthalpy of solvation of the hydrogen atom, $\Delta H_{solv}^{A}(H^{\bullet})$ (=2 kcal mol^{-1}), and the enthalpy of hydrogen bond formation between phenol and each of these two solvents, ΔH_{28}^{A}(PhOH- - -A) (=4.7 kcal mol^{-1} in both cases), we obtain the "true" O−H bond dissociation energy for phenol, BDE(O−H)^{gas} = 88.3 kcal mol^{-1} (see column 5 of Table 4). These two BDE(O−H)^{gas} values and the values obtained in isooctane, CCl_4, and benzene (see column 5) are equal within experimental error to the value from gas-phase measurements, viz., ca. 87 kcal mol^{-1} (see Table 1).

Post facto, eq 29 is eminently reasonable since it implies that the measured O−H BDE for phenol in solution will increase as the HBA ability of the solvent increases. In condensed

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(34) An error of 0.03 in the quantum yield, Φ_9, would produce an error of ca. 0.5 kcal mol^{-1} in BDE (O−H), while an error of 0.02 in f_{obs} would produce an error of ca. 1.5 kcal mol^{-1}. This is because while the absolute errors in f_{obs} and $1 - f_{obs}$ are the same, the relative error in $1 - f_{obs}$ is much greater.

(35) A reviewer has suggested that the gas phase be used to define the standard state for the hydrogen atom which has the advantage that eq 27 simplifies to $\mathrm{BDE(O{-}H)^{gas}} - \mathrm{BDE(O{-}H)^{A}} = \Delta H_{solv}^{A}(\mathrm{PhOH}) - \Delta H_{solv}^{A}(\mathrm{PhO}^{\bullet})$ However, the thermodynamic formalism requires that the standard states of all species (PhOH, PhO•, and H•) are in the same medium.

(36) See, e.g.: (a) Powell, D. L.; West, R. *Spectrochim. Acta* **1964**, *20*, 983−991. (b) Arnett, E. M.; Jaris, L.; Mitchell, E. J.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1970**, *92*, 2365−2377. (c) Gramstad, T.; Sandström, J. *Spectrochim. Acta* **1969**, *25A*, 31−38. (d) Jawed, I. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2602−2605. (e) Elpy, T. D.; Drago, R. S. *J. Am. Chem. Soc.* **1967**, *89*, 5770−5773. (f) Sousa Lopez, M. C.; Thompson, H. W. *Spectrochim. Acta* **1968**, *24A*, 1367−1383. (g) Arnett, E. M.; Mitchell, E. J.; Murty, T.S.S.R. *J. Am. Chem. Soc.* **1974**, *96*, 3875−3891.

(37) Nielsen, M. F. *Acta Chem. Scand.* **1992**, *46*, 533−548. Nielsen, M. F.; Hammerich, O. *Acta Chem. Scand.* **1992**, *46*, 883−896.

media, the simple fact is that the *apparent* O−H bond strength for phenol and structurally related compounds will be lowest in a nonpolar, nonpolarizable medium (e.g., saturated hydrocarbon, lipid, etc.) and will be considerably higher in a polar medium containing strong hydrogen bond acceptors (e.g., water). This, in turn, means that the kinetics (rates) of radical trapping by phenols will be highly dependent on the medium in which the measurements are made;[16,38] hydrogen bonding reduces the amount of free phenol and hence the apparent rate constant for hydrogen atom abstraction is lower in HBA solvents.[16]

Some Comments on the Use of the EC Method To Determine BDEs. The foregoing discussion suggests that BDE values in HBA solvents can be derived from gas-phase values provided the hydrogen bond enthalpy is known. Moreover, the increase in the magnitude of $\mathrm{BDE(O{-}H)^{sol}}$ when the solvent (A) is replaced by a stronger HBA solvent (A′) will simply be equal to the increase in the enthalpy of formation of the hydrogen bond to A′ compared with A (eq 30).

$$\mathrm{BDE(O{-}H)^{A'}} - \mathrm{BDE(O{-}H)^{A}} = \Delta H_{28}{}^{\mathrm{A'}}(\mathrm{PhOH\text{-}\text{-}\text{-}A'}) - \Delta H_{28}{}^{\mathrm{A}}(\mathrm{PhOH\text{-}\text{-}\text{-}A}) \quad (30)$$

The dearth of gas-phase data has prompted the development of a number of experimental alternatives for the measurement or estimation of BDE values. Among the most useful of these is the thermochemical cycle approach developed by Bordwell[41] and Arnett[42] in which electrode potentials and pK_a values are combined to give the gas-phase BDEs according to eq 31. In this equation the magnitude of the constant, *C*, was derived empirically and was found to be 73.3 kcal mol^{-1} (referenced to the ferrocene/ferrocenium couple).[41]

$$\mathrm{BDE(R{-}H)^{gas}} = 1.37\mathrm{p}K_\mathrm{a} + 23.06E^\circ + C \quad (31)$$

While there can be fairly good agreement between bond strengths derived using this EC approach and gas-phase measurements, there are some limitations to the EC method which result from the attempt to use solution *free energy* measurements to obtain gas-phase *enthalpies*. Although some of these problems have been discussed previously by Parker,[3b] it would appear that further elaboration is still necessary. Wayner and Parker[3a] derived the explicit thermodynamic relationship between the solution bond dissociation *free energy*, $\Delta G^\circ_\mathrm{BDE}(\mathrm{R{-}H})$, the p$K_a$(R−H), and electrode potentials for oxidation of R$^-$,$E^\circ(\mathrm{R^\bullet/R^-})$ and the reduction of H$^+$,$E^\circ(\mathrm{H^+/H^\bullet})$ (eq 32).

$$\Delta G^\circ{}_\mathrm{BDE}(\mathrm{R{-}H}) = 1.37\mathrm{p}K_\mathrm{a} - 23.06\{E^\circ(\mathrm{H^+/H^\bullet}) - \mathrm{E}^\circ(\mathrm{R^\bullet/R^-})\} \quad (32)$$

Combining eq 29 with the corresponding entropy terms leads to eq 33 which, when combined with eq 32, can be rearranged to the form of eq 31 (eq 34).

$$\Delta G^\circ{}_\mathrm{BDE}(\mathrm{R{-}H}) = \mathrm{BDE(R{-}H)^{gas}} + \Delta H_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) + \Delta H_{28}{}^\mathrm{A}(\mathrm{R{-}H\text{-}\text{-}\text{-}A}) - T\{\Delta S_\mathrm{BDE}{}^\mathrm{gas} + \Delta S_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) + \Delta S_{28}{}^\mathrm{A}(\mathrm{R{-}H\text{-}\text{-}\text{-}A})\} \quad (33)$$

$$\mathrm{BDE(R{-}H)^{gas}} = 1.37\mathrm{p}K_\mathrm{a} + 23.06E^\circ(\mathrm{R^\bullet/R^-}) + T\{\Delta S_\mathrm{BDE}{}^\mathrm{gas} + \Delta S_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) + \Delta S_{28}{}^\mathrm{A}(\mathrm{R{-}H\text{-}\text{-}\text{-}A})\} - \Delta H_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) - \Delta H_{28}{}^\mathrm{A}(\mathrm{R{-}H\text{-}\text{-}\text{-}A}) - 23.06E^\circ(\mathrm{H^+/H^\bullet}) \quad (34)$$

The empirical equation derived by Bordwell[41] was based only on R−H compounds which do not hydrogen bond and hence, in eq 31, the value of the constant, *C*, does not include any contribution from hydrogen bonding. Using data from the literature,[3] the value of this constant can be *calculated* to be 76.2 kcal mol^{-1} at 298 K (eq 35) (referenced to the ferrocene/ferrocenium couple) which is acceptably close to the *empirical* value of 73.3 kcal mol^{-1}. (The 3 kcal mol^{-1} difference between the calculated and empirical values of *C* probably arises from the fact that the empirical value was derived using peak potentials that were not corrected for homogeneous or heterogeneous kinetic effects). However, for phenol and other hydrogen bond donors it will be obvious that *C* will no longer be solvent independent (eq 36).

$$C = T\{\Delta S_\mathrm{BDE}{}^\mathrm{gas} + \Delta S_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet})\} - \Delta H_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) - 23.06E^\circ(\mathrm{H^+/H^\bullet}) \quad (35)$$

$$C^\mathrm{A} = T\{\Delta S_\mathrm{BDE}{}^\mathrm{gas} + \Delta S_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) + \Delta S_{28}{}^\mathrm{A}(\mathrm{R{-}H\text{-}\text{-}\text{-}A})\} - \Delta H_\mathrm{solv}{}^\mathrm{A}(\mathrm{H^\bullet}) - \Delta H_{28}{}^\mathrm{A}(\mathrm{R{-}H\text{-}\text{-}\text{-}A}) - 23.06E^\circ(\mathrm{H^+/H^\bullet}) \quad (36)$$

Using these ideas, it is possible to calculate $\mathrm{BDE(O{-}H)^{DMSO}}$ for phenol in DMSO which was the solvent used by Bordwell[5] for the electrochemistry and pK_a measurements, viz.,

$$\mathrm{BDE(PhO{-}H)^{DMSO}} = \mathrm{BDE(PhO{-}H)^{gas}} + \Delta H_\mathrm{solv}{}^\mathrm{DMSO}(\mathrm{H^\bullet}) + \Delta H_{28}{}^\mathrm{DMSO}(\mathrm{PhOH\text{-}\text{-}\text{-}DMSO}) = 87 + 2.0 + 6.6 = 95.6\ \mathrm{kcal\ mol^{-1}} \quad (37)$$

The reported values for phenol in the "gas phase" using data from DMSO[5] and sulfolane[6] are 89.9 and 91.6 kcal mol^{-1}, respectively (see Table 1). However, based on the foregoing discussion it is clear that because the authors used the empirical eq 31 they failed to properly account for the solvent effect. For DMSO, the correction to the constant, *C*,[36b] decreases the derived values by ca. 3.5 kcal mol^{-1} so that the modified values, using the data reported by Bordwell[5] and Arnett,[6] become 86.4 and 88.1 kcal mol^{-1}, respectively (assuming that hydrogen bonding in sulfolane is similar to that in DMSO). Both of these values are acceptably close to the recommended gas-phase value (see Table 1). Of equal concern is the fact that for a series of phenols having various pK_a's the hydrogen bond energies are almost certain to vary. Thus, there are likely to be systematic errors for BDE(O−H) values measured by the EC method in DMSO which have been reported for families of phenols[43] simply because C^DMSO(ArOH) will *not be constant*.

To summarize, and in agreement with the guidelines set out by Griller and co-workers,[32] any determination of BDE(X−

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[38] In a hydrocarbon solvent the rate constant for peroxyl radical trapping by α-tocopherol (vitamin E) is $3.2 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$,[39] but this value drops to $2.3 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ in *tert*-butyl alcohol.[40]

[39] Burton, G. W.; Doba, T.; Gabe, E. J.; Hughes, L.; Lee, F. L.; Prasad, L.; Ingold, K.U. *J. Am. Chem. Soc.* **1985**, *107*, 7053−7065.

[40] Barclay, L. R. C.; Baskin, K. A.; Locke, S. J.; Schaefer, T. D. *Can. J. Chem.* **1987**, *65*, 2529−2540.

[41] Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510−517 and references cited therein.

[42] Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J. P. *Science* **1990**, *247*, 423−430 and references cited therein.

[43] Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736−1743.

H)^{sol} will include both the homolytic cleavage of the X−H bond and the loss of hydrogen bonding. This is true irrespective of the technique used to measure BDE(O−H)^{sol}, i.e., it will apply to the PAC method as well as the EC method.

Experimental Section

All solvents were of spectroscopic quality and used as received unless otherwise noted. Phenol (Merck) was purified by recrystallization (three times) from the melt in hexane. Cyclohexadiene (Aldrich or Janssen, 97%) was used as received. *o*-Hydroxybenzophenone (Aldrich or Janssen) was recrystallized three times from ethanol. Di-*tert*-butyl peroxide was passed over activated alumina prior to use.

Photoacoustic Calorimetry. Two instruments were used for these studies and gave the same results. One of these (Leiden) consists of a standard fluorescence cuvette (Hellma 221), modified to allow for continuous flow experiments, containing solutions of di-*tert*-butyl peroxide and phenol in the solvent of interest. After deoxygenation by purging with argon, the solutions were photolyzed using 600-ps pulses from a PRA LN 1000 nitrogen laser (337.1 nm, 84.8 kcal mol^{-1}). The resulting shock wave was detected by a piezo electric transducer (Panametrics Model V101, 0.5 MHz) in contact with the bottom of the cell (a thin layer of vacuum grease ensured good acoustic transmission). The signals were amplified (Panametrics Model 5670 ultrasonic preamp) and digitized (Tektronix Model 2430A Digital Oscilloscope). The signal-to-noise ratio was improved by signal averaging. Fluctuations in the laser energy were monitored using a L-PED pyroelectric device to which 10% of the incident laser beam was directed. The remaining radiation was passed through a 1 mm pin-hole. The average laser energy in these experiments was $<50\ \mu$J/pulse (i.e., flux < 6 mJ/cm^2). The photoacoustic cell was located inside a HP Model 8452A diode array spectrophotometer so that the absorbance of the solution could be measured simultaneously. The instrument was calibrated using either ferrocene or *o*-hydroxybenzophenone in solutions that contained all of the components in the solvent of interest except the peroxide. The other instrument (Ottawa) has been described in detail elsewhere.[2,17] The only difference is that a Laser Photonics Model VSL 337ND nitrogen laser was used.

Quantum Yields. In order to minimize the formation of light absorbing products resulting from air oxidation of the solvents, solutions of DTBP were prepared by weight in volumetric flasks purged with argon using deaerated solvents. Test solutions contained either (a) DTBP (0.5−0.7 M) and two GC standards (benzene and chlorobenzene or benzonitrile and chlorobenzene) or (b) an actinometry standard (Aberchrome 540 in toluene or azoxybenzene in 95% ethanol, 2−4 mM). The use of two GC standards improved the precision of the determination of the very small quantities of *tert*-butyl alcohol produced in the photolysis (HP Model 5890 equipped with a HP Model 7673A automatic injector.). In a typical experiment, 2 mL of a test solution was placed in a standard 1 cm path length cuvette which was equipped with a magnetic stirrer to ensure sample homogeneity. The optical density of the solution was measured (HP Model 8452 UV−vis spectrophotometer) and the cuvette was then placed in a metal holder containing a 5 mm × 5 mm hole. The solution was then subjected to irradiation from a nitrogen laser (Molectron UV-20, 337 nm, 10 Hz, defocused to give ca. 1 mJ cm^2 per pulse) for an interval between 10 and 30 min after which a 1-μL sample was removed for GC analysis. A plot of [*tert*-butyl alcohol] versus time was linear for $<2\%$ conversion of the DTBP. After each interval the number of absorbed photons was determined by subjecting a solution of the actinometer to the laser irradiation for between 3 and 5 min. A plot of OD$_{494}$ or OD$_{458}$ for Aberchrome 540 or azoxybenzene, respectively, also was linear and constant for the duration of the experiment.

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