Solvation Enthalpies of Free Radicals: O−O Bond Strength in Di-*tert*-butylperoxide

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Abstract: The photolysis reaction of di-*tert*-butylperoxide was studied in various solvents by photoacoustic calorimetry (PAC). This technique allows the determination of the enthalpy of this homolysis reaction, which by definition corresponds to the O−O bond dissociation enthalpy of the peroxide in solution, DH^{o}_{sln}(O−O). The derived value from these experiments in benzene, 156.7 ± 9.9 kJ mol^{-1}, is very similar to a widely accepted value for the gas-phase bond dissociation enthalpy, DH^{o}(O−O) = 159.0 ± 2.1 kJ mol^{-1}. However, when the PAC-based value is used together with auxiliary experimental data and Drago's ECW model to estimate the required solvation terms, it leads to 172.3 ± 10.2 kJ mol^{-1} for the gas-phase bond dissociation enthalpy. This result, significantly higher than the early literature value, is however in excellent agreement with a recent gas-phase determination of 172.5 ± 6.6 kJ mol^{-1}. The procedure to derive the gas-phase DH^{o}(O−O) was tested by repeating the PAC experiments in carbon tetrachloride and acetonitrile. The average of the values thus obtained was DH^{o}(O−O) = 179.6 ± 4.5 kJ mol^{-1}, confirming that the early gas-phase result is a lower limit. More importantly, the present study questions the usual assumption that the solvation terms of homolysis reactions producing free radicals in solution should cancel, and suggests a methodology to estimate solvation enthalpies of free radicals.

Introduction

The standard solvation enthalpy of a substance AB, $\Delta_{sln}H^{o}$(AB,g), is defined as the standard enthalpy associated with the dissolution of gaseous AB in a given solvent, usually at 298.15 K.

$$AB(g) \rightarrow AB(sln) \qquad (1)$$

Solvation enthalpies are commonly determined as the difference between two quantities, obtained from separate experiments and different techniques. The first of those quantities, $\Delta_{sln}H^{o}$(AB,cr/l), is the standard solution enthalpy of crystalline or liquid AB in the solvent (see eq 2); the second quantity, $\Delta_{sub/vap}H^{o}$(AB,cr/l), is the standard sublimation or vaporization enthalpy of AB.

$$\Delta_{sln}H^{o}(AB,g) = \Delta_{sln}H^{o}(AB,cr/l) - \Delta_{sub/vap}H^{o}(AB,cr/l) \qquad (2)$$

Standard calorimetric techniques can be used to measure both terms in eq 2.[1] Alternatively, $\Delta_{sub/vap}H^{o}$(AB,cr/l) can be obtained by a vapor pressure vs temperature plot.[1] In either case, the final value of $\Delta_{sln}H^{o}$(AB,g) can be known with an error smaller than ca. 1 kJ mol^{-1}.

While the application of eq 2 is straightforward for many long-lived species, it has never been used to evaluate solvation enthalpies of free radicals, simply because the available experimental techniques are not suited to deal with transient species. This accounts for the scarcity of solvation energetics data for free radicals, despite their importance. The strategy to obtain the solvation enthalpy of a free radical must therefore rely on a different approach. Usually, this strategy consists simply in comparing the enthalpy of a reaction where the radical is a reactant or a product with the enthalpy of the same reaction in solution. This involves, of course, the use of several gas-phase and solution experimental techniques. There are some examples where this approach could be followed. For instance, in a molecule AH, the measurement of the oxidation potential of A^{-} coupled with the pK_a of AH and auxiliary data yields the A−H bond dissociation enthalpy in solution, DH^{o}_{sln}(A−H).[2] On the other hand, the measurements of the acidity of AH and the adiabatic electron affinity of A afford the gas-phase A−H bond dissociation enthalpy, DH^{o}(A−H).[3] Unfortunately, however, the solution methodology involves auxiliary data and assumptions that are controversial. Hence, the absolute values of DH^{o}_{sln}(A−H) may be affected by significant errors. To avoid these errors, the "electrochemical" method is usually calibrated by using gas-phase results.

Photoacoustic calorimetry (PAC) is probably the most reliable method for obtaining solution-phase bond dissociation enthalpies.[4] Surprisingly, however, the results from this technique were seldom used to derive information on free radical solvation energetics. Exceptions include an early study by Kanabus-

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[1] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

[2] Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510.

[3] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[4] Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342.

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Scheme 1

$$t\text{-BuOOBu-}t(\text{sln}) \xrightarrow{h\nu} 2\ t\text{-BuO}^{\bullet}(\text{sln}) \qquad (3)$$

$$2\text{PhOH}(\text{sln}) + 2\ t\text{-BuO}^{\bullet}(\text{sln}) \rightarrow 2\text{PhO}^{\bullet}(\text{sln}) + 2\ t\text{-BuOH}(\text{sln}) \qquad (4)$$

$$t\text{-BuOOBu-}t(\text{sln}) + 2\text{PhOH}(\text{sln}) \rightarrow 2\text{PhO}^{\bullet}(\text{sln}) + 2\ t\text{-BuOH}(\text{sln}) \qquad (5)$$

Kaminska et al.,[5] where the solvation enthalpies of carbon-centered radicals were investigated, and three more recent publications where the solvation of phenoxy radicals is discussed.[6−8]

In the present paper we wish to report our studies on the solvation of *tert*-butoxyl radical, a species that is often used as a reactant in photoacoustic calorimetric experiments.

Results and Discussion

A widely accepted value for the oxygen−oxygen gas-phase bond dissociation enthalpy in di-*tert*-butylperoxide, 159.0 ± 2.1 kJ mol^{-1}, relies on the determination of the activation energy for the O−O bond homolysis of that compound.[9] This result was very recently corroborated by another study using the same method, yielding 162.8 ± 2.1 kJ mol^{-1},[10] but given the agreement between the two values, we will refer only to the first one in the following discussion.[11] To compare gas-phase and solution energetics of that bond, we decided to use photoacoustic calorimetry to determine the bond dissociation enthalpy of di-*tert*-butylperoxide in solution, $DH^{\circ}_{\text{sln}}(\text{O−O})$. This involves measuring the enthalpy of reaction 3 (Scheme 1) in the photoacoustic calorimeter (see Experimental Section), which can be directly identified with $DH^{\circ}_{\text{sln}}(\text{O−O})$. The application of the PAC technique to the general problem of the determination of bond dissociation enthalpies has been described in detail[6,8] and is beyond the scope of the present paper. However, a brief description is useful to highlight the importance of di-*tert*-butylperoxide in those studies. The approach is illustrated in Scheme 1, using the O−H bond in phenol as an example, where the photochemically produced *tert*-butoxyl radical is employed to break the bond of interest, yielding PhO$^{\bullet}$.

The O−H bond dissociation enthalpy in phenol, DH°_{sln}(PhO−H), can be derived from the enthalpy of the net reaction 5 in Scheme 1, $\Delta_r H$. The relationship can be established from a thermodynamic cycle, yielding eq 6, which contains several solution enthalpy terms ($\Delta_{\text{sln}}H$) and enthalpies of formation. These auxiliary data are available from the literature,[8] and some were subject to a recent reevaluation.[12,13]

$$\begin{aligned} DH^{\circ}_{\text{sln}}(\text{PhO−H}) = {} & \Delta_r H/2 + \Delta_f H^{\circ}(\text{H}^{\bullet},\text{g}) + \Delta^{\circ}_{\text{sln}}H(\text{H}^{\bullet},\text{g}) + \\ & \Delta_f H^{\circ}(t\text{-BuOOBu-}t,\text{l})/2 - \Delta_f H^{\circ}(t\text{-BuOH},\text{l}) + \\ & \Delta_{\text{sln}}H^{\circ}(t\text{-BuOOBu-}t,\text{l})/2 - \Delta_{\text{sln}}H^{\circ}(t\text{-BuOH},\text{l}) \quad (6) \end{aligned}$$

The PAC technique allows the determination of the net reaction enthalpy, $\Delta_r H$, through a simple energy balance. Part of the energy of the absorbed laser photons (e.g., $E_m = 354.87$ kJ mol^{-1} for a nitrogen laser) is used to cleave the O−O bond in *t*-BuOOBu-*t*, thus initiating the reaction. The remaining laser energy, in this example increased by the exothermicity of the fast hydrogen abstraction in reaction 4, is deposited as heat in solution and produces a shock wave. This heat ($\Delta_{\text{obs}}H$), which can be determined because it is proportional to the wave amplitude, is then related, by eq 7, to the enthalpy of the net reaction 5 (Φ_r is the quantum yield of reaction 3).

$$\Delta_r H = \frac{E_m - \Delta_{\text{obs}}H}{\Phi_r} + \frac{\Delta_r V}{\chi} \qquad (7)$$

The last term in eq 7 represents a correction due to the so-called nonthermal expansion. If a reaction is accompanied by a nonnegligible molar volume change ($\Delta_r V$), as in the case of reaction 5, a fraction of the observed wave amplitude will be due to that physical expansion; i.e., the true value of the heat deposition will be less than the one observed. This, in turn, implies a positive correction of $\Delta_r H$. The parameter χ is the adiabatic expansion coefficient of the solvent and depends (eq 8) on its thermoelastic properties, namely the isobaric expansion coefficient, α_p, the heat capacity, C_p, and the density, ρ.

$$\chi = \frac{\alpha_p}{\rho C_p} \qquad (8)$$

In the present example, the volume change of the net reaction 5 is assumed to be equal to the volume change for the homolysis of the di-*tert*-butylperoxide alone, since the volume change for reaction 4 should be negligible.

The focus of the present paper is the homolysis of di-*tert*-butylperoxide alone. It is now clear that this work is intimately linked with the broader experimental procedure illustrated above. In both studies, eq 7 (with the same auxiliary values Φ_r and $\Delta_r V$) can be used to determine the enthalpy of the overall reaction in solution (3 and 5, respectively). In the first case, the reaction enthalpy corresponds directly to the bond dissociation enthalpy of di-*tert*-butylperoxide in solution.

We started our work by studying reaction 3 in benzene. Using the estimated value of $\Delta_r V = 13.4 \pm 4$ mL mol^{-1},[6,14] $\Delta_r H = DH^{\circ}_{\text{sln}}(\text{O−O})$ was calculated through eq 7. The results, displayed in Table 1, are in very good agreement with the values recalculated from another PAC study in benzene.[15]

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

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

[7] de Heer, M. I.; Korth, H.-G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969.

[8] Borges dos Santos, R. M.; Lagoa, A. L. C.; Martinho Simões, J. A. *J. Chem. Thermodyn.* **1999**, *31*, 1483.

[9] (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F. *NIST Chemical Kinetics Database*, version 6.0; NIST Standard Reference Data, National Institute of Standards and Technology: Gaithersburg, MD, 1994.

[10] Reints, W.; Pratt, D. A.; Korth, H.-G.; Mulder, P. *J. Phys. Chem. A* **2000**, *104*, 10713.

[11] The authors in ref 10 claim that the reliability of their value for DH°(O−O), and thus for $\Delta_f H^{\circ}(t\text{-BuO}^{\bullet}, \text{g})$, is supported by the excellent agreement between their result derived for DH°(*t*-BuO−H) and the one recommended in the literature (Stein, S. E.; Rukkers, J. M.; Brown, R. L. *NIST Structures and Properties Database*, version 2.0; NIST Standard Reference Data; National Institute of Standards and Technology: Gaithersburg, MD, 1994). However, the agreement is not surprising since the literature value relies on the results reported in ref 9a. This reference and the work by Reints et al. report very similar DH°(O−O) values.

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

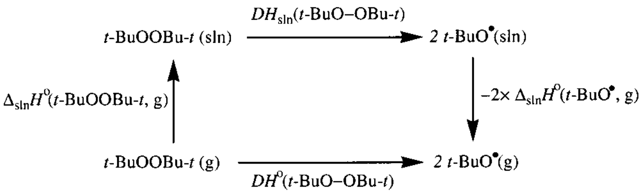
[13] Wayner et al.[6] established an alternative method to the one based on the direct thermodynamic cycle illustrated by eq 6. Using an auxiliary reaction, those authors avoided the need for thermochemical data on di-*tert*-butylperoxide and *tert*-butyl alcohol, including its solution enthalpies, in eq 6. Their method relies, however, on the C−H bond dissociation enthalpy in 1,4-dicyclohexadiene. Both methods give equivalent results.[8] It should also be stressed that both eq 6 and the alternative method do not require the value of the O−O bond dissociation enthalpy in di-*tert*-butylperoxide (see, however, note 14).

Table 1. PAC Determination of Solution Bond Enthalpies, $DH^{o}_{sln}(O-O)$, for Di-*tert*-butylperoxide in Various Solvents

solvent	$\Delta_{obs}H$ (kJ mol^{-1})	Φ_r[a]	χ[b] (mL kJ^{-1})	$DH^{o}_{sln}(O-O)$ (kJ mol^{-1})
C_6H_6	238.7 ± 7.1[c]	0.83	0.799	156.7 ± 9.9
	235.6 ± 7.5[d]			160.5 ± 10.3
CCl_4	241.4 ± 4.0[c]	0.76	0.907	164.1 ± 6.9
	241.0 ± 8.4[e]			164.6 ± 11.9
	246.7 ± 8.4[f]			157.1 ± 11.9
CH_3CN	230.4 ± 3.3[c]	0.89	0.791	156.8 ± 6.3

[a] From ref 6. [b] Data used to calculate χ from Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; Wiley: New York, 1986. [c] This work. Average of at least five independent determinations. The experimental uncertainties are twice the standard deviation of the mean in each case. [d] Reference 15. [e] Burkey, T. J.; Majewsky, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218. [f] Calculated from data in ref 6.

Scheme 2



The value obtained for $DH^{o}_{sln}(O-O)$ in benzene, 156.7 ± 9.9 kJ mol^{-1}, is very similar to the gas-phase result presented above, 159.0 ± 2.1 kJ mol^{-1}, suggesting that the solvation effects involved in reaction 3 should cancel. However, to further investigate this matter, we need to consider the solvation terms that relate $DH^{o}_{sln}(O-O)$ to $DH^{o}(O-O)$. These terms are shown in Scheme 2.

In the case of the peroxide, $\Delta_{sln}H^{o}$(t-BuOOBu-t,g) could be easily obtained (see eq 2) as −38.1 ± 1.0 kJ mol^{-1} through experimental determinations of its vaporization enthalpy, $\Delta_{vap}H^{o}$-(*t*-BuOOBuO-*t*) = 39.3 ± 1.0 kJ mol^{-1},[12] and its solution enthalpy in benzene, $\Delta_{sln}H^{o}$(*t*-BuOOBu-*t*,l)= 1.21 ± 0.22 kJ mol^{-1}.[8] To estimate $\Delta_{sln}H^{o}$(t-BuO$^{\bullet}$,g), we have used the electrostatic−covalent model, also known as the ECW model, developed by Drago and co-workers, which permits calculation of the difference between the solvation enthalpies of *tert*-butyl alcohol and *tert*-butoxyl radical in benzene.[16] This procedure is similar to the one used to estimate the same difference for phenol and phenoxyl radical, illustrated in the recent literature.[8,17] For instance, solvents such as carbon tetrachloride, a weak Lewis base, will have negligible interactions both with *t*-BuOH and *t*-BuO$^{\bullet}$, so that $\Delta_{sln}H^{o}$(*t*-BuOH,g) − $\Delta_{sln}H^{o}$(*t*-BuO$^{\bullet}$,g) ≈ 0. On the other hand, a strong Lewis base solvent like acetonitrile, which is also a hydrogen bond acceptor, is able to form one hydrogen bond with *t*-BuOH. The same conclusion can be drawn for a weaker hydrogen bond acceptor like benzene. The enthalpy of this hydrogen bond will therefore be a good approximation of the difference $\Delta_{sln}H^{o}$(*t*-BuOH,g) − $\Delta_{sln}H^{o}$(*t*-BuO$^{\bullet}$,g). By providing an estimation for the enthalpy of this hydrogen bond, the ECW model is a convenient procedure to derive that difference. It relies on eq 9, which contains four parameters that reflect electrostatic (E_AE_B) and covalent (C_AC_B) contributions to the enthalpies of donor−acceptor interactions. Donor (B) and acceptor (A) parameters, optimized by a large database of experimentally determined enthalpies, are available for many substances.[16]

Table 2. Determination of Gas-Phase Bond Enthalpies, $DH^{\circ}(O-O)$, for Di-*tert*-butylperoxide from Solution Data (Values in kJ mol^{-1})

solvent	$\Delta_{sln}H^{\circ}$ (*t*-BuOOBu0*t*,l)[a]	$\Delta_{sln}H^{\circ}$ (*t*-BuOH,l)[a]	ΔH (ECW)[b]	DH° (O−O)
C_6H_6	1.21 ± 0.22	15.5 ± 0.4	−4.4	172.3 ± 10.2
CCl_4	0.35 ± 0.04	16.2 ± 1.0	0 [c]	186.1 ± 7.5
CH_3CN	5.5 ± 0.2	10.2 ± 0.5	−9.2	177.6 ± 6.7

[a] Obtained by reaction-solution calorimetry. Average of at least five independent results. The uncertainties are twice the standard deviation of the mean in each case. [b] Enthalpy for hydrogen bond formation between *tert*-butyl alcohol and the solvent using the ECW model (see text). [c] By definition.

$$-\Delta H(\mathrm{ECW}) = E_AE_B + C_AC_B \qquad (9)$$

The ECW model predicts that the difference ΔH(ECW) = $\Delta_{sln}H^{o}$(*t*-BuOH,g) − $\Delta_{sln}H^{o}$(*t*-BuO$^{\bullet}$,g) = −4.4 kJ mol^{-1} in benzene. This result, together with $\Delta_{sln}H^{o}$(*t*-BuOH,l) = 15.50 ± 0.35 kJ mol^{-1},[8] and $\Delta_{vap}H^{o}$(*t*-BuOH) = 46.7 ± 0.1 kJ mol^{-1},[18] leads to $\Delta_{sln}H^{o}$(*t*-BuO$^{\bullet}$,g) = −26.8 kJ mol^{-1} in benzene, with an uncertainty estimated as ca. 1 kJ mol^{-1}.

The above solvation enthalpy data and the PAC value for $DH^{o}_{sln}(O-O)$ in benzene allow the determination of $DH^{o}(O-O)$ using eq 10 (or Scheme 2). This procedure leads to 172.3 ± 10.2 kJ mol^{-1} for the gas-phase O−O bond dissociation enthalpy in di-*tert*-butylperoxide (Table 2), which is some 13 kJ mol^{-1} higher than the presently accepted value.

$$DH^{o}(O-O) = DH^{o}_{sln}(O-O) + \Delta_{sln}H^{o}(t\text{-BuOOBu-}t\text{,g}) - 2\Delta_{sln}H^{o}(t\text{-BuO}^{\bullet}\text{,g}) \qquad (10)$$

Recent energy-resolved threshold collision-induced (TCID) experiments, by DeTuri and Ervin,[19] afforded the gas-phase acidities of several alcohols, including *tert*-butyl alcohol. These results were coupled with very accurate values for the adiabatic electron affinities of the alkoxyl radicals,[20] yielding gas-phase O−H bond dissociation enthalpies at 298.15 K. In the case of *t*-BuOH, $DH^{o}(O-H)$ = 446 ± 3 kJ mol^{-1}, together with the gas-phase standard enthalpies of formation of the alcohol (−312.5 ± 0.8 kJ mol^{-1})[18] and the peroxide (−341.5 ± 2.2 kJ mol^{-1}),[12] implies Δ_fH^{o}(*t*-BuO$^{\bullet}$,g) = −84.5 ± 3.1 kJ mol^{-1} and $DH^{o}(O-O)$ = 172.5 ± 6.6 kJ mol^{-1}. This value is in excellent agreement with the PAC result and the ECW model to estimate the solvation enthalpy of *tert*-butoxyl radical.

To further test the combined PAC−ECW method, we have repeated the determination of $DH^{o}(O-O)$ using carbon tetrachloride and acetonitrile as solvents. The same procedure

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(14) An important feature of the indirect method of Wayner et al.[6] is that it also avoids the need to correct for the reaction volume change. Yet, for the PAC study of the simpler reaction addressed here, this estimative is unavoidable. Those authors also made a critical assessment of Δ_rV, recommending the value used in the present paper. Interestingly, this value was based on the assumption that the "old" $DH^{o}(O-O)$ for di-*tert*-butylperoxide is identical in solution. Although this is not true, as demonstrated by our results, it was a fortunate choice because that early gas-phase value is very close to $DH^{o}_{sln}(O-O)$.

(15) Clark, K. B.; Wayner, D. D. M.; Demirdji, S. H.; Koch, T. H. *J. Am. Chem. Soc.* **1993**, *115*, 2447.

(16) (a) Drago, R. S.; Dadmun, A. P.; Vogel, G. C. *Inorg. Chem.* **1993**, *32*, 2473. (b) Vogel, G. C.; Drago, R. S. *J. Chem. Educ.* **1996**, *73*, 701−707. (c) Drago, R. S. *Applications of Electrostatic−Covalent Models in Chemistry*; Surfside: Gainesville, FL, 1994.

(17) Bizarro, M. M.; Costa Cabral, B. J.; Borges dos Santos, R. M.; Martinho Simões, J. A. *Pure Appl. Chem.* **1999**, *71*, 1249.

(18) Pedley, J. B. *Thermodynamic Data and Structures of Organic Compounds*, Vol. 1; Thermodynamics Research Center: College Station, TX, 1994.

(19) DeTuri, V. F.; Ervin, K. M. *J. Phys. Chem. A* **1999**, *103*, 6911.

(20) Ramond, T. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C. *J. Chem. Phys.* **2000**, *112*, 1158.

outlined above for benzene was followed, and the results are summarized in Tables 1 and 2.

To discuss the final results, it is important to consider the uncertainties involved. First, it should be noted that the main contribution to the overall uncertainty in the present study comes from the PAC result ($\Delta_{obs}H$), which can easily ascend to ca. 8 kJ mol^{-1}.[21] The cumulative error from the correction to the gas phase should be less than 3 kJ mol^{-1}. It can be argued that our result in benzene, 172.3 ± 10.2 kJ mol^{-1}, is not significantly different from the early gas-phase value of DH^o(O−O) = 159.0 ± 2.1 kJ mol^{-1}. Indeed, the magnitude of the error bar in our result brings the two values very close together. However, the results obtained from the experiments in carbon tetrachloride and acetonitrile, which, within their uncertainties, agree with the one obtained from the benzene experiments, clearly favor the "high" value for the gas-phase O−O bond dissociation enthalpy in the peroxide: the average of those three results is DH^o(O−O) = 179.6 ± 4.5 kJ mol^{-1}.

Although the DH^o(O−O) value obtained from the study in carbon tetrachloride agrees, within the error bars, with those derived from the experiments in the other solvents, a significant discrepancy is still apparent. This may be partly caused by the correction ΔH(ECW) = $\Delta_{sln}H^o$(*t*-BuOH,g) − $\Delta_{sln}H^o$(*t*-BuO$^\bullet$,g), which was estimated to be zero. However, the reasonable assumption of a small interaction through hydrogen bond formation, e.g., −2 kJ mol^{-1}, will decrease DH^o(O−O) in Table 2 by 4 kJ mol^{-1}.

The lowest of the three values, obtained from the studies in benzene, may also be affected by shortcomings in the ΔH(ECW) correction. There is spectral evidence that the *tert*-butoxyl radical forms π-complexes with electron-rich aromatic molecules.[22] This interaction was first suggested by observing that the characteristic "tail-end" absorption in the near UV of these radicals is red-shifted in aromatic solvents such as benzene, relative to those in nonaromatic solvents such as carbon tetrachloride and acetonitrile. This was then tested by a spectroscopic search of such a complex. When the above radicals were generated in the presence of 1,3,5-trimethoxybenzene, a charge-transfer absorption was observed in the visible region (440 nm). This band confirmed the formation of the π-complex between the radical and the electron-rich aromatic, which shifts the absorption into the visible. The interaction between the *tert*-butoxyl radical and benzene must then be considered when evaluating the magnitude of $\Delta_{sln}H^\circ$(*t*−BuOH,g) − $\Delta_{sln}H^o$(*t*-BuO$^\bullet$,g) in that solvent. This difference should correspond to the hydrogen bond formation between *tert*-butyl alcohol and benzene, estimated by the ECW model, *minus* the enthalpy of the interaction between the radical and the solvent (also negative), which is not contemplated in that model. This leads to a more positive value than the one used, −4.4 kJ mol^{-1}, thus bringing the final value of DH^o(O−O) derived from the benzene studies closer to the other two.

The enthalpy of hydrogen bonding between *tert*-butyl alcohol and the solvent, identified with the difference $\Delta_{sln}H^o$(*t*-BuOH,g) − $\Delta_{sln}H^o$(*t*-BuO$^\bullet$,g), which is central to our calculation of gas-phase values from solution studies, can be obtained by a procedure alternative to the ECW model. A method developed by Abraham et al.,[23] based on relative hydrogen bond acceptor and donor properties, was recently extended by Snelgrove et al.[24] to allow a quantitative description of the kinetic solvent effect on the rate of hydrogen atom abstraction by radicals. This extension of Abraham's method can also be used to derive the Gibbs energy for hydrogen bonding, thus providing an alternative estimate for the above difference, with an estimated error of ±1 kJ mol^{-1}.[25] Using this procedure, as outlined in ref 24, one obtains −2.1, −0.76, and −6.7 kJ mol^{-1} for the Gibbs energy of hydrogen bond *formation* between *tert*-butyl alcohol and the solvents benzene, carbon tetrachloride, and acetonitrile, respectively. The corresponding gas-phase DH^o(O−O) values are 176.9 ± 10.2, 184.6 ± 7.5, and 182.6 ± 6.7 kJ mol^{-1}, respectively, with an average of 182.2 ± 4.5 kJ mol^{-1}.

The main conclusion of the previous exercise is that the two methods to estimate $\Delta_{sln}H^o$(*t*-BuOH,g) − $\Delta_{sln}H^o$(*t*-BuO$^\bullet$,g) yield essentially the same results. However, it is noted that the method proposed by Snelgrove et al.[24] leads to a better overall agreement between the final gas-phase values obtained from the different solution studies, and to an even higher value for the average gas-phase O−O bond dissociation enthalpy. The improvement of the overall agreement can partly be explained by noting that the procedure proposed by Snelgrove et al. includes an interaction between *tert*-butyl alcohol and carbon tetrachloride, based on experimental evidence that this compound acts as an hydrogen bond acceptor relative to alkanes.[24]

A fundamental difference between Drago's model and the procedure proposed by Snelgrove et al. is that the former is based on enthalpies of complexation, whereas the latter is derived from equilibrium constants of hydrogen bond acidity and basicity, hence providing estimates of Gibbs energy changes. Despite the somewhat better agreement obtained with the method proposed by Snelgrove et al., the ECW model may provide better estimates, simply because it directly affords the *enthalpy* of the hydrogen bond. Nevertheless, it is reassuring that both methods afforded essentially the same results and conclusions and may be used in future studies to complement each other.

The early gas-phase literature value DH^o(O−O) = 159.0 ± 2.1 kJ mol^{-1}, which is based on activation energy data for the homolysis of di-*tert*-butylperoxide, is some 20 kJ mol^{-1} *lower* than the result found in our studies. Although those data, as listed in the *NIST Chemical Kinetics* Database,[9b] vary between 130 and 163 kJ mol^{-1}, and the corresponding *A* factors vary by a few orders of magnitude, most results lie in a narrower range (E_a= 155−162 kJ mol^{-1} and $A = 10^{15}-10^{16}$ s^{-1}), so that the correct value for the activation energy is likely to be close to 159 kJ mol^{-1}. The source of the discrepancy may therefore be related to the method used to extract the O−O bond dissociation enthalpy at 298 K from an activation energy obtained from measurements at higher temperatures (typically, 400−500 K). This method relies on several assumptions, including the structure of the transition state and the assumption that the recombination of the *tert*-butoxyl radicals has a negligible activation energy.[9a] Hence, the disagreement between the "low" and the "high" values for DH^o(O−O) may be caused by a larger-than-expected temperature correction to E_a (i.e., the activation enthalpy at 298 K would be considerably higher than that at 400−500 K) and/or by a *negative* activation energy for the

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[21] This is *twice* the standard deviation associated with $\Delta_{obs}H$. In many literature studies this thermochemical convention is not followed; i.e., the errors are reported as the standard deviations.

[22] Avila, D. V.; Ingold, K. U.; Di Nardo, A. A.; Zerbetto, F.; Zgiersky, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711. We thank a reviewer for pointing out these results to us.

[23] (a) Abraham, M. H.; Priscilla, L. G.; Prior, D. V.; Duce, P. P.; Morris, J. J.; Taylor, P. J *J. Chem. Soc., Perkin Trans. 2* **1989**, 699. (b) Abraham, M. H.; Priscilla, L. G.; Prior, D. V.; Morris, J. J.; Taylor, P. J *J. Chem. Soc., Perkin Trans. 2* **1990**, 521.

[24] Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P. Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469.

[25] We are indebted to a reviewer for illustrating this alternative method for us.

recombination of *tert*-butoxyl radicals. These questions deserve to be further investigated.

Conclusion

Photoacoustic calorimetry studies combined with the ECW model led to 179.6 ± 4.5 kJ mol^{-1} for the gas-phase O−O bond dissociation enthalpy of di-*tert*-butylperoxide. This result is significantly higher than the widely accepted gas-phase literature value (159.0 ± 2.1 kJ mol^{-1}) but supports another gas-phase value, derived from acidity and electron affinity data (172.5 ± 6.6 kJ mol^{-1}). The procedure proposed in the present study allows estimating the solvation of free radicals energetics and indicates that the frequent assumption of canceling solvation enthalpies must be used with caution. The procedure is based on simple thermodynamic cycles, involving quantities easily determined by well-established experimental techniques, and on the ECW model.

Experimental Section

All solvents were of spectroscopic or HPLC grade and used as received. Di-*tert*-butylperoxide (Aldrich) was purified according to a literature procedure.[12] *o*-Hydroxybenzophenone (Aldrich) was recristalized twice from an ethanol−water mixture.

The auxiliary solution enthalpies of *tert*-butyl alcohol and di-*tert*-butylperoxide were determined at $T = 298.15$ K in a reaction-solution calorimeter described elsewhere.[26]

Photoacoustic Calorimetry. Both the photoacoustic calorimeter setup and the experimental technique have been described in detail.[8] Briefly, a ca. 0.4 M solution of argon-purged di-*tert*-butylperoxide in the appropriate solvent was flowed through a standard quartz flow cell (Hellma 174-QS), where it was irradiated with pulses from a nitrogen laser (PTI PL 2300, 337.1 nm, pulse width 800 ps, ca. 5−30 μJ/pulse at the cell, flux < 40 J m^{-2}). Each pulse produced photolysis of the peroxide, and the resulting wave was detected by a piezoelectric transducer (Panametrics V101, 0.5 MHz) in contact with the bottom of the cell. The signals were amplified (Panametrics 5662) and measured by a digital oscilloscope (Tektronix 2430A). The apparatus was calibrated by carrying out a photoacoustic run using an optically matched (within 1−2% absorbance units at 337.1 nm) solution of *o*-hydroxybenzophenone, which dissipates all of the absorbed energy as heat.[27]

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[26] (a) Diogo, H. P. Tese de Doutoramento, Instituto Superior Técnico, Lisboa, Portugal, 1993. (b) Leal, J. P.; Pires de Matos, A.; Martinho Simões, J. A. *J. Organomet. Chem.* **1991**, *403*, 1.

[27] An important requirement of the PAC technique is that the thermoelastic properties of the solution used in the calibration and those of the sample solution, namely their adiabatic expansion coefficient χ (eq 8), should be identical. Since the solutions used are normally very diluted, it is generally assumed that both will have χ equal to that of the pure solvent. There has been a nagging doubt as to whether this assumption is valid for the experiments based on the approach illustrated in Scheme 1, due to the fact that the sample solution contains ca. 7% (v/v) of di-*tert*-butylperoxide, whereas the calibration contains none. The same doubt applies to the experiments reported in this paper. We are currently investigating this matter by determining experimental values of χ for the solutions involved. However, all the available evidence seems to corroborate the assumption: (1) the shape and time-of-flight of the photoacoustic waveform are the same for calibration and experiment; (2) increasing the amount of peroxide in the sample solution does not noticeably affect the time-of-flight of the photoacoustic waveform; (3) a plot of the photoacoustic signal versus the amount of peroxide added during the experiment remains linear even beyond 12% (v/v) of peroxide in solution (ref 8, see also Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746).