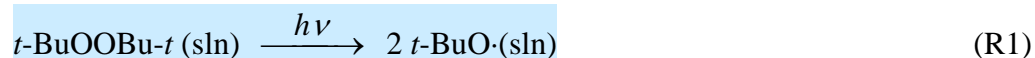


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Di-*tert*-butylperoxide O–O BDE, in selected solvents

The PAC study of reaction



yields ϕ_{obs} .

The reaction enthalpy of reaction R1, $\Delta_r H$, is calculated using the following equations and values:

$$\Delta_{\text{obs}} H = \phi_{\text{obs}} E_m, \quad (1)$$

(where the laser energy of our nitrogen laser is $E_m = 354.87 \text{ kJ mol}^{-1}$)

$$\Delta_r H = \frac{E_m - \Delta_{\text{obs}} H}{\Phi_r} + \frac{\Delta_r V}{\chi}, \quad (2)$$

$$\chi = \frac{\alpha_p}{\rho C_p}, \quad (3)$$

The reaction volume change, independent of solvent, is $\Delta_r V = 13.4 \pm 4 \text{ mL mol}^{-1}$.¹ Finally,

$$DH_{\text{sln}}^{\circ}(\text{O} - \text{O}) = \Delta_r H.$$

Table 1 PAC determination of solution bond dissociation enthalpies, $DH_{\text{sln}}^{\circ}(\text{O} - \text{O})$, for di-*tert*-butylperoxide in several solvents.

solvent	$\Delta_{\text{obs}} H / \text{kJ mol}^{-1}$	Φ_r ¹	$\chi / \text{mL kJ}^{-1}$ ²	$DH_{\text{sln}}^{\circ}(\text{O} - \text{O}) / \text{kJ mol}^{-1}$
C ₆ H ₆	238.7 ± 7.1 ³	0.83	0.799	156.7 ± 9.9
	235.6 ± 7.5 ⁴			160.5 ± 10.3
CCl ₄	241.4 ± 4.0 ³	0.76	0.907	164.1 ± 6.9
	241.0 ± 8.4 ⁵			164.6 ± 11.9
	246.7 ± 8.4 ¹			157.1 ± 11.9
CH ₃ CN	230.4 ± 3.3 ³	0.89	0.791	156.8 ± 6.3

***tert*-Butyl alcohol O–H BDE, in selected solvents**

The enthalpy of formation of the *tert*-butoxyl radical in solution can be derived from the O–O bond dissociation enthalpy of di-*tert*-butylperoxide in solution, using the following equations:

$$DH_{\text{sln}}^{\circ}(\text{O} - \text{O}) = 2\Delta_{\text{f}}H^{\circ}(t\text{-BuO}^{\bullet}, \text{sln}) - \Delta_{\text{f}}H^{\circ}(t\text{-BuOOBu-}t, \text{sln}) \quad (4)$$

$$\Delta_{\text{f}}H^{\circ}(t\text{-BuOOBu-}t, \text{sln}) = \Delta_{\text{f}}H^{\circ}(t\text{-BuOOBu-}t, \text{l}) + \Delta_{\text{sln}}H^{\circ}(t\text{-BuOOBu-}t, \text{l}) \quad (5)$$

The solution O–H bond dissociation enthalpy in *tert*-butyl alcohol can then be obtained from the following set of equations, recalling its definition: $t\text{-BuO–H}(\text{sln}) \rightarrow t\text{-BuO}^{\bullet}(\text{sln}) + \text{H}^{\bullet}(\text{sln})$

$$DH_{\text{sln}}^{\circ}(t\text{-BuO–H}) = \Delta_{\text{f}}H^{\circ}(t\text{-BuO}^{\bullet}, \text{sln}) + \Delta_{\text{f}}H^{\circ}(\text{H}^{\bullet}, \text{sln}) - \Delta_{\text{f}}H^{\circ}(t\text{-BuOH}, \text{sln}) \quad (6)$$

$$\Delta_{\text{f}}H^{\circ}(t\text{-BuOH}, \text{sln}) = \Delta_{\text{f}}H^{\circ}(t\text{-BuOH}, \text{l}) + \Delta_{\text{sln}}H^{\circ}(t\text{-BuOH}, \text{l}) \quad (7)$$

$$\Delta_{\text{f}}H^{\circ}(\text{H}^{\bullet}, \text{sln}) = \Delta_{\text{f}}H^{\circ}(\text{H}^{\bullet}, \text{g}) + \Delta_{\text{sln}}H^{\circ}(\text{H}^{\bullet}, \text{g}) \quad (8)$$

Table 2 Auxiliary values of enthalpies of formation and solution. Data in kJ mol⁻¹.

compound, state	$\Delta_{\text{f}}H^{\circ}$	$\Delta_{\text{sln}}H^{\circ}$ ³		
		C ₆ H ₆	CCl ₄	CH ₃ CN
<i>t</i> -BuOOBu- <i>t</i> , l	-380.9±0.9 ⁶	1.21±0.22	0.35±0.04	5.5±0.2
<i>t</i> -BuOH, l	-359.2±0.8 ⁶	15.5±0.4	16.2±1.0	10.2±0.5
H [•] , g	217.998±0.006 ⁷		5±1 ^a	

^a Average value in organic solvents. ^{8,9}

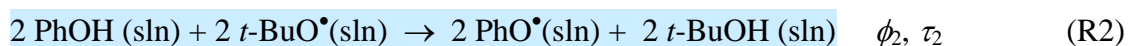
Table 3 Determination of enthalpies of formation of *tert*-butoxy radical in several solvents, $\Delta_{\text{f}}H^{\circ}(t\text{-BuO}^{\bullet}, \text{sln})$ and solution bond dissociation enthalpies for *tert*-butyl alcohol, $DH_{\text{sln}}^{\circ}(t\text{-BuO–H})$. Data in in kJ mol⁻¹.

solvent	$DH_{\text{sln}}^{\circ}(\text{O} - \text{O})$ ^a	$\Delta_{\text{f}}H^{\circ}(t\text{-BuO}^{\bullet}, \text{sln})$	$DH_{\text{sln}}^{\circ}(t\text{-BuO–H})$
C ₆ H ₆	156.7±9.9	-111.5±5.0	455.2±5.2
CCl ₄	164.1±6.9	-108.2±3.5	457.8±3.8
CH ₃ CN	156.8±6.3	-109.3±3.2	462.7±3.5

^a cf. Table 1.

TR-PAC determination of solution phase BDEs

The reactions below exemplify the two-step sequence analysed by TR-PAC for the determination of the phenol O–H bond dissociation enthalpy in solution:



Deconvolution analysis yields the amplitudes, ϕ_1 and ϕ_2 , of each step, and the lifetime, τ_2 , of the second. Only the thermochemical result for the second step is needed.

The reaction enthalpy of the second step, $\Delta_r H_2$, is calculated by (cf. eqs 1 and 2):

$$\Delta_r H_2 = \frac{-\Delta_{\text{obs}} H_2}{\Phi_r} \quad (\text{note that } \Delta_r V_2 = 0)^1 \quad (9)$$

Φ_r values in selected solvents were presented in Table 1.

The desired BDE is given by:

$$DH_{\text{sln}}^\circ (\text{PhO} - \text{H}) = \Delta_r H_2 / 2 + DH_{\text{sln}}^\circ (t\text{-BuO} - \text{H}) \quad (10)$$

$DH_{\text{sln}}^\circ (t\text{-BuO} - \text{H})$ for selected solvents were presented in Table 3.

Relative BDEs

Substituent effects are often evaluated in relation to a reference molecule. For a substituted phenolic compound, ArOH, the relevant quantity is $\Delta DH^\circ (\text{ArO} - \text{H})$, the *relative* BDE, which is defined as the difference between the absolute BDEs:

$$\Delta DH_{\text{sln}}^\circ (\text{ArO} - \text{H}) = DH_{\text{sln}}^\circ (\text{ArO} - \text{H}) - DH_{\text{sln}}^\circ (\text{PhO} - \text{H}) \quad (11)$$

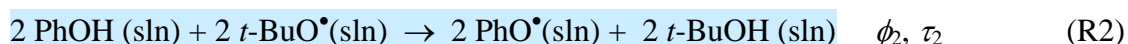
Denoting by $\Delta_r H'_2$ the enthalpy of reaction R2 for ArOH, obtained from a separate TR-PAC experiment, relative BDEs can then be calculated by:

$$\Delta DH_{\text{sln}}^\circ (\text{ArO} - \text{H}) = \Delta_r H'_2 / 2 - \Delta_r H_2 / 2 = (\Delta_{\text{obs}} H_2 - \Delta_{\text{obs}} H'_2) / (2\Phi_r)$$

or
$$\Delta DH_{\text{sln}}^\circ (\text{ArO} - \text{H}) = (\phi_2 - \phi'_2) E_m / (2\Phi_r) \quad (12)$$

Single experiment TR-PAC determination of solution phase BDEs

The reactions below exemplify the two-step sequence analysed by TR-PAC for the determination of the phenol O–H bond dissociation enthalpy in solution:



Deconvolution analysis yields the amplitudes, ϕ_1 and ϕ_2 , of each step, and the lifetime, τ_2 , of the second. The thermochemical results from both steps allow the determination of the desired BDE in the *actual* experimental solution.

First, recal the relation between the solution BDEs of O–H in *tert*-butyl alcohol and O–O in di-*tert*-butylperoxide (introduce eqs 4,5,7, and 8 in 6):

$$\begin{aligned} DH_{\text{sln}}^\circ(t\text{-BuO-H}) &= DH_{\text{sln}}^\circ(\text{O-O})/2 \\ &+ [\Delta_f H^\circ(t\text{-BuOOBu-}t, \text{l}) + \Delta_{\text{sln}} H^\circ(t\text{-BuOOBu-}t, \text{l})]/2 \\ &+ \Delta_f H^\circ(\text{H}^\bullet, \text{g}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) - \Delta_f H^\circ(t\text{-BuOH, l}) - \Delta_{\text{sln}} H^\circ(t\text{-BuOH, l}) \end{aligned} \quad (13)$$

Then, given that $DH_{\text{sln}}^\circ(\text{O-O}) = \Delta_r H_1$ and introducing 13 in 10, one obtains:

$$\begin{aligned} DH_{\text{sln}}^\circ(\text{PhO-H}) &= (\Delta_r H_1 + \Delta_r H_2)/2 \\ &+ \Delta_f H^\circ(t\text{-BuOOBu-}t, \text{l})/2 - \Delta_f H^\circ(t\text{-BuOH, l}) + \Delta_f H^\circ(\text{H}^\bullet, \text{g}) \\ &+ \Delta_{\text{sln}} H^\circ(t\text{-BuOOBu-}t, \text{l})/2 - \Delta_{\text{sln}} H^\circ(t\text{-BuOH, l}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) \end{aligned} \quad (14)$$

Finally, using the solvent-independent values from Table 2,⁶⁻⁹ we obtain:

$$\begin{aligned} DH_{\text{sln}}^\circ(\text{PhO-H}) &= (1 - \phi_1 - \phi_2)E_m / (2\Phi_r) + \Delta_r V_1 / (2\chi) + (386.75 \pm 1.02) \\ &+ \Delta_{\text{sln}} H^\circ(t\text{-BuOOBu-}t, \text{l})/2 - \Delta_{\text{sln}} H^\circ(t\text{-BuOH, l}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) \end{aligned} \quad (15)$$

Note that all terms in eq 15 refer to the same TR-PAC experiment, i.e., to the same solution (cf. Effect of di-*tert*-butylperoxide, and Quantum yield estimates).

TR-PAC determination of enthalpies of formation of radicals in solution

The enthalpy of formation of the phenoxy radical in solution is related to the O–H BDE of the parent compound PhOH in solution by:

$$\Delta_f H^\circ(\text{PhO}^\bullet, \text{sln}) = DH_{\text{sln}}^\circ(\text{PhO}-\text{H}) + \Delta_f H^\circ(\text{PhOH}, \text{sln}) - \Delta_f H^\circ(\text{H}^\bullet, \text{sln}) \quad (16)$$

The O–H BDE of phenol in solution is derived from the TR-PAC experiment by eq 10.

Now, substituting eq 4 into 6:

$$DH_{\text{sln}}^\circ(t-\text{BuO}-\text{H}) = \left[DH_{\text{sln}}^\circ(\text{O}-\text{O}) + \Delta_f H^\circ(t-\text{BuOOBu}-t, \text{sln}) \right] / 2 + \Delta_f H^\circ(\text{H}^\bullet, \text{sln}) - \Delta_f H^\circ(t-\text{BuOH}, \text{sln}) \quad (17)$$

And then substituting eq 17 into 10, and the result into eq 16, one obtains:

$$\Delta_f H^\circ(\text{PhO}^\bullet, \text{sln}) = \Delta_f H_2 / 2 + \left[DH_{\text{sln}}^\circ(\text{O}-\text{O}) + \Delta_f H^\circ(t-\text{BuOOBu}-t, \text{sln}) \right] / 2 - \Delta_f H^\circ(t-\text{BuOH}, \text{sln}) + \Delta_f H^\circ(\text{PhOH}, \text{sln}) \quad (18)$$

Values of $\Delta_f H^\circ(t-\text{BuOOBu}-t, \text{sln})$ and $\Delta_f H^\circ(t-\text{BuOH}, \text{sln})$ for selected solvents are calculated from eqs 5 and 7, respectively. $\Delta_f H^\circ(\text{PhOH}, \text{sln})$ is calculated in a similar manner with $\Delta_{\text{sln}} H^\circ(\text{PhOH}, \text{cr})$ in benzene ($18.6 \pm 0.6 \text{ kJ mol}^{-1}$)¹⁰ or acetonitrile ($9.2 \pm 0.2 \text{ kJ mol}^{-1}$),¹⁰ and using $\Delta_f H^\circ(\text{PhOH}, \text{cr}) = -165.1 \pm 0.7 \text{ kJ mol}^{-1}$.⁶

Using TR-PAC results from single experiment:

Substituting 15 into 16, and using $\Delta_f H^\circ(\text{H}^\bullet, \text{g})$ from Table 2 and $\Delta_f H^\circ(\text{PhOH}, \text{cr})$ from above, one obtains:

$$\Delta_f H^\circ(\text{PhO}^\bullet, \text{sln}) = (1 - \phi_1 - \phi_2) E_m / (2\Phi_r) + \Delta_f V_1 / (2\chi) + (3.7 \pm 1.2) + \Delta_{\text{sln}} H^\circ(t-\text{BuOOBu}-t, \text{l}) / 2 - \Delta_{\text{sln}} H^\circ(t-\text{BuOH}, \text{l}) + \Delta_{\text{sln}} H^\circ(\text{PhOH}, \text{cr}) \quad (19)$$

As in eq 15, all terms in eq 19 correspond to the actual TR-PAC experimental solution.

Note that the enthalpy of formation of radicals in solution derived by TR-PAC, either with eq 18 or 19, *does not depend* on any assumption regarding solvation of radicals.

**Effect of di-*tert*-butylperoxide on solvation enthalpies
in TR-PAC experiments ¹¹**

Table 4 Solution enthalpies of di-*tert*-butylperoxide and *tert*-butanol, determined by reaction-solution calorimetry. Data in kJ mol⁻¹.³

solvent	$\Delta_{\text{sln}}H^\circ(t\text{-BuOOBu-}t, l)$	$\Delta_{\text{sln}}H^\circ(t\text{-BuOH}, l)$
C ₆ H ₆	1.21±0.22	15.5±0.4
CCl ₄	0.35±0.04	16.2±1.0
CH ₃ CN	5.5±0.2	10.2±0.5

Table 5 Solution enthalpies of di-*tert*-butylperoxide and *tert*-butanol in the the actual TR-PAC experimental solutions (without peroxide!), determined by reaction-solution calorimetry.

solvent	[PhOH] mM	$\Delta_{\text{sln}}H^\circ(t\text{-BuOOBu-}t, l)$ kJ mol ⁻¹	$\Delta_{\text{sln}}H^\circ(t\text{-BuOH}, l)$ kJ mol ⁻¹
C ₆ H ₆	3.0	1.46±0.08	14.50±0.74
CCl ₄	1.4	0.29±0.15	
CH ₃ CN	94.0	5.43±0.36	9.84±0.64

Table 6 Solution enthalpies of di-*tert*-butylperoxide and *tert*-butanol in the actual TR-PAC experimental solutions, determined by reaction-solution calorimetry.

solvent	[PhOH] mM	$\Delta_{\text{sln}}H^\circ(t\text{-BuOOBu-}t, l)^a$ kJ mol ⁻¹	$\Delta_{\text{sln}}H^\circ(t\text{-BuOH}, l)^a$ kJ mol ⁻¹
C ₆ H ₆	3.0	1.51±0.16	15.55±0.28
CCl ₄	1.4	0.17±0.08	16.8±0.9
CH ₃ CN	94.0	5.33±0.14	9.51±0.3

^a Solution enthalpies in a solution containing the indicated phenol concentration and ca. 4-7% of di-*tert*-butylperoxide.

Quantum yield estimates

The quantum yields (Φ_r) for photolysis of di-*tert*-butylperoxide in various solvents have been determined by actinometry (Table 7). The fraction of *tert*-butoxy radical pairs that are trapped in the solvent cage, $1 - \Phi_r$, decreases as the solvent viscosity, η , decreases¹² (Figure 1 and equation 20). The quantum yield in mixtures can be estimated using eq 20 with the mass average of the viscosities of the components.¹³

Table 7 Variation of the quantum yield (Φ_r) for the photolysis of di-*tert*-butylperoxide with the viscosity (η) of the solvent (at 298 K).

solvent	Φ_r ¹	$\eta / (\text{g m}^{-1}\text{s}^{-1})^2$
hexane	0.93	0.2942
acetonitrile	0.89	0.3410
heptane	0.85	0.3967
benzene	0.83	0.6028
nonane	0.81	0.6696

$$\frac{1}{(1-\Phi_r)} = (5.46 \pm 0.25) + \frac{(4.35 \pm 3.65) \times 10^{-3}}{\eta^{(6.23 \pm 0.68)}} \quad (20)$$

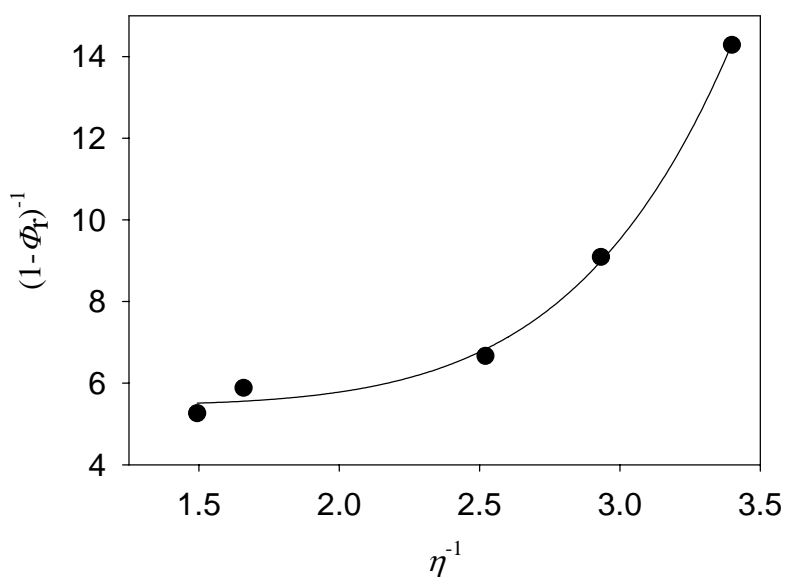


Figure 1 Plot of data from Table 7, fitted with eq 20.

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