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Energetics of Alkylbenzyl Radicals: A Time-Resolved Photoacoustic Calorimetry Study

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Received: August 5, 2003; In Final Form: October 16, 2003

The PhCH₂–H bond dissociation enthalpy in solution was determined for the first time as 380.5 ± 5.1 kJ mol⁻¹, from a time-resolved photoacoustic calorimetry study (TR–PAC) in toluene. The derived gas-phase result, 375.5 ± 5.0 kJ mol⁻¹, allows the calculation of the enthalpy of formation of the benzyl radical as $\Delta_f H^\circ(\text{PhCH}_2^\bullet, \text{g}) = 208.0 \pm 5.0$ kJ mol⁻¹, which is in excellent agreement with a value recently published in the literature, obtained from gas-phase experiments, and demonstrates the accuracy of TR–PAC as a tool for the study of organic radical energetics. A detailed discussion of the methods and assumptions used to derive those values from the TR–PAC experiments was made. The study was then extended to ethylbenzene and cumene. The results support the assumption that solvation enthalpies of the alkylbenzenes and their corresponding radicals are similar. The trend of C–H bond dissociation enthalpies in those alkylbenzenes is in keeping with early gas-phase literature results, but it is in clear contrast with the values obtained from a proton affinity cycle using data from the NIST Chemistry WebBook.

Introduction

Photoacoustic calorimetry (PAC) is a technique that is being increasingly applied to determine bond dissociation enthalpies in solution,¹ and recent developments have improved our knowledge on the solvation corrections needed to relate solution and gas-phase data.^{2–5} However, the PAC technique employed in most studies has an important limitation: it can only be used if the radical of interest is generated through a suitably fast reaction. Usually, this involves hydrogen abstraction from an appropriate substrate with photochemically produced *tert*-butoxy radicals, in a process with an overall duration in the nanosecond time scale. Although procedures using auxiliary reactions can be used to circumvent this limitation,⁶ a simpler, more direct approach exists: it consists of a development of the original technique, which affords not only thermochemical but also kinetic information. This version of the technique is called time-resolved photoacoustic calorimetry (TR–PAC) and was first used to study the energetics of radicals in solution by Peters and co-workers.⁷ Surprisingly, in addition to this pioneering work, TR–PAC was seldom applied to study the energetics of organic free radicals, contrasting with its use for organometallic compounds.⁸

In this work we used time-resolved photoacoustic calorimetry to determine, primarily, the enthalpy of formation of the benzyl radical, PhCH₂[•], a key compound in radical chemistry.⁹ Three main reasons motivated our present studies: (1) the reported experimental results for the enthalpy of formation of PhCH₂[•] at 298.15 K rely mainly on gas-phase kinetic studies involving high temperatures (in the range of ca. 1000–1500 K).^{10,11} Thus, a direct measurement at 298.15 K would allow to assess the temperature corrections used in the gas-phase studies. (2) Although it is not simple to probe the energetics of benzyl

radical with the classical version of PAC (also called “static”), the required TR–PAC experiment is of the most straightforward type that can be devised with this technique. We thus feel that this study is also a good example to illustrate the strength of the TR–PAC approach to the study of the energetics of organic free radicals. (3) To further demonstrate the general applicability of the technique, the TR–PAC procedure was then extended to the determination of the enthalpy of formation of two other alkylbenzyl radicals: ethylbenzyl (PhCH[•]CH₂CH₃) and cumyl (PhC[•](CH₃)₂). The gas-phase results that can be derived from literature data for these two species are not entirely consistent.^{12–14}

Experimental Section

Materials. Benzene (Aldrich, HPLC grade, 99.9+ %), toluene (Aldrich, HPLC grade, 99.8%), ethylbenzene (Aldrich, GC grade, 99%), and cumene (Aldrich, GC grade, 99%) were all used as received. Di-*tert*-butylperoxide (Aldrich) was purified according to a literature procedure.¹⁵ *ortho*-Hydroxybenzophenone (Aldrich) was recrystallized twice from an ethanol–water mixture.

Photoacoustic Calorimetry. The basis of photoacoustic calorimetry has been widely discussed before,^{7,16,17} and only a brief outline is given here. The PAC technique involves the measurement of a volume change that occurs when a laser pulse strikes a solution containing the reactants and initiates a chemical reaction. This sudden volume change generates an acoustic wave, which can be recorded by a sensitive microphone such as an ultrasonic transducer. The resulting photoacoustic signal, S , is defined by eq 1, where T is the solution transmittance, E is the incident laser energy, and K is a calibration constant, dependent on the instrumental specifications and geometry and on the thermoelastic properties of the solution.

$$S = K\phi_{\text{obs}}(1 - T)E \quad (1)$$

The parameter ϕ_{obs} is the apparent fraction of photon energy

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released as heat which, when multiplied by the molar energy of the laser photons ($E_m = N_A h\nu$), corresponds to the measured apparent enthalpic change, $\Delta_{\text{obs}}H$. It has been shown that ϕ_{obs} consists of a thermal contribution, due to the enthalpy of the reaction, and a reaction volume contribution, due to the differences between the partial molar volumes of the reactants and products.¹⁸ The latter leads to the introduction of a correction factor when calculating the reaction enthalpy through an energy balance,^{17,19} eq 2.

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

In this equation, Φ_r represents the reaction quantum yield. The correction term includes the reaction volume change, $\Delta_r V$, and the adiabatic expansion coefficient of the solution, χ . Since the solutions used are usually very diluted, this parameter depends on the thermoelastic properties of the solvent, namely the isobaric expansion coefficient, α_p , the heat capacity, C_p , and the density, ρ , eq 3.

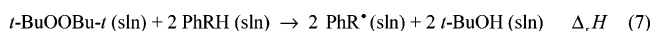
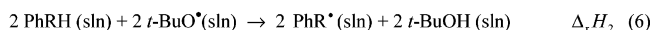
$$\chi = \frac{\alpha_p}{\rho C_p} \quad (3)$$

Equation 1 is the basis of “classical” photoacoustic calorimetry, usually called non-time-resolved PAC (in the sense that the time dependence of the signal S is not analyzed; see below). Its application is valid only when the process generating the photoacoustic signal is much faster than the transducer response.²⁰ In this case, the time profile of the photoacoustic wave will depend only on the instrumental response and not on the rate of the process, allowing the direct correspondence between its amplitude S and the apparent heat fraction ϕ_{obs} . On the other hand, processes that are much slower than the transducer response will give rise to virtually no signal. In the intermediate regime, each process with a different rate will originate a unique waveform. For instance, in a system where one or more of such processes occur, the signal obtained will be a convoluted waveform that will appear phase shifted and reduced in amplitude due to the presence of components corresponding to slower reactions. A deconvolution analysis of such data yields the magnitude of each of the signal-inducing events (as well as information on their rates).²¹ This is the basis of time-resolved photoacoustic calorimetry (TR-PAC). The analysis involves the normalization of the photoacoustic waveform for its respective absorbance ($1-T$) and incident laser energy E , as indicated in eq 1. Extraction of ϕ_{obs} for the process(es) is then accomplished by the deconvolution of the waveform, facilitated by the use of commercially available software.²² Reaction enthalpies for each process are then calculated as before.^{16b} For instance, considering a two-step sequential reaction, the enthalpy of the first step is given by eq 2 (with $\Delta_{\text{obs}}H = \Delta_{\text{obs}}H_1$, calculated from the amplitude $\phi_{\text{obs},1}$ obtained from the deconvolution, and $\Delta_r V = \Delta_r V_1$). The enthalpy of the second step is calculated with eq 4 (note that only the first step is light-initiated but the yield of all the steps is dependent on the quantum yield for the first one).

$$\Delta_r H_2 = \frac{-\Delta_{\text{obs}}H_2}{\Phi_r} + \frac{\Delta_r V_2}{\chi} \quad (4)$$

In this work we used the time-resolved version of the photoacoustic calorimetry technique (TR-PAC). The photoacoustic calorimeter setup and experimental procedure have been described in detail elsewhere.^{5,17} Briefly, argon-purged solutions

SCHEME 1



in benzene of ca. 0.4 M of di-*tert*-butylperoxide and each alkylbenzene in the adequate concentration (see Results and Discussion) were flowed through a quartz flow cell (Hellma 174-QS). The solutions were photolyzed with pulses from a nitrogen laser (PTI PL 2300, 337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral density filters (ca. 5–30 $\mu\text{J/pulse}$ at the cell, flux < 40 J m^{-2}). Each pulse induced a volume change in solution, producing an acoustic wave which 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 signal-to-noise ratio was improved by averaging 32 acquisitions. To check for multiphoton effects, each data point, at each of four different incident laser energies used, was determined five times and the average was plotted against laser energy. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched (within typically 5% absorbance units at 337.1 nm) solution of *ortho*-hydroxybenzophenone (which dissipates all of the absorbed energy as heat) in the same mixtures, but without the peroxide. For each run (experiment or calibration), four data points were collected, corresponding to the four different laser intensities obtained using neutral density filters. The resulting waveforms from each data point were recorded for subsequent mathematical analysis, affording three waveforms for each point: sample, calibration, and pure solvent (pure toluene or, for each alkylbenzene, a solution in benzene). After the normalization of the waveforms (see above), the analysis for each point involved the subtraction of the solvent signal from both the sample and calibration waveforms²³ and then their deconvolution using the software Sound Analysis by Quantum Northwest.²²

Reaction-Solution Calorimetry. The enthalpies of solution of *tert*-butyl alcohol and *tert*-butyl peroxide in toluene were determined with an isoperibol reaction-solution calorimeter.²⁴ Solute concentrations varied between 2×10^{-3} M and 6×10^{-3} M of *tert*-butyl alcohol and between 1×10^{-3} M and 2×10^{-3} M of *tert*-butyl peroxide. The results refer also to 298 K and represent the average of five (*tert*-butyl alcohol) or four (*tert*-butyl peroxide) independent experiments. The uncertainties are twice the standard deviation of the mean in each case.

Results and Discussion

The set of reactions that were examined by photoacoustic calorimetry are shown in Scheme 1. A *tert*-butoxy radical generated from the photolysis of di-*tert*-butylperoxide (reaction 5) abstracts a hydrogen from the alkylbenzene substrate (PhRH), yielding the corresponding benzylic radical (reaction 6). Reaction 7 represents the net process.

The slower process in Scheme 1 is the abstraction of the benzylic hydrogen from the alkylbenzene (reaction 5 is, in practical terms, instantaneous). In toluene, the rate constant for this process in benzene is $2.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$,²⁵ which, for our 0.5 MHz transducer, renders the overall reaction too slow to be studied by static PAC. In fact, even when neat toluene is used, this process falls in the intermediate regime. TR-PAC must

then be applied.²⁶ Deconvolution of the photoacoustic waveforms obtained in this case affords the amplitudes (ϕ_{obs}) of the two elementary steps in Scheme 1 and the lifetime (τ) of the second.^{16b} In the present case, we are mainly interested in reaction 6. Its enthalpy ($\Delta_r H_2$) can be calculated from eq 8, derived from eq 4 by assuming that the volume change is negligible, which is sensible because the hydrogen abstraction is a metathesis reaction.² It should be pointed out that this represents a further advantage of TR-PAC over classical PAC, since it allows us to avoid the volume correction presented in eq 2 (however, see below). Φ_r is the *t*-BuO-OBu-*t* homolysis quantum yield in the respective solution.²⁷

$$\Delta_r H_2 = -\Delta_{\text{obs}} H_2 / \Phi_r \quad (8)$$

As the enthalpy of reaction 6 is simply twice the difference between the C-H bond dissociation enthalpy of the alkylbenzene and the O-H bond dissociation enthalpy of *tert*-butyl alcohol, both in solution, $DH_{\text{sln}}^\circ(\text{C} - \text{H})$ can be derived from eq 9.

$$DH_{\text{sln}}^\circ(\text{C} - \text{H}) = \Delta_r H_2 / 2 + DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H}) \quad (9)$$

To determine the O-H bond dissociation enthalpy of *tert*-butyl alcohol in solution, several approaches can be used. The first one uses the gas-phase value reported by DeTuri and Ervin,²⁸ $DH^\circ(t\text{-BuO} - \text{H}) = 444.9 \pm 2.8 \text{ kJ mol}^{-1}$, as the starting point. To estimate $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H})$ from that value, three solvation terms are needed, according to eq 10.

$$DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H}) = DH^\circ(t\text{-BuO} - \text{H}) - \Delta_{\text{sln}} H^\circ(t\text{-BuOH}, \text{g}) + \Delta_{\text{sln}} H^\circ(t\text{-BuO}^\bullet, \text{g}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) \quad (10)$$

The solvation of the hydrogen atom can be estimated using the hydrogen molecule as a suitable model,²⁹ yielding $\Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) = 5 \pm 1 \text{ kJ mol}^{-1}$ for organic solvents.³⁰ The solvation terms for *tert*-butyl alcohol and *tert*-butoxy radical are still required, but only the former is experimentally available. In a recent work, this problem was solved by adopting a procedure based on Drago's ECW model³¹ to estimate solvation terms of free radicals.^{4,5} This model contains four parameters that reflect electrostatic ($E_A E_B$) and covalent ($C_A C_B$) contributions to the enthalpies of donor-acceptor interactions (eq 11).

$$-\Delta H(\text{ECW}) = E_A E_B + C_A C_B \quad (11)$$

Donor (B) and acceptor (A) parameters, optimized by a large database of experimentally determined enthalpies, are available for many substances.³¹ One can then use this model to obtain the enthalpy of the hydrogen bond, $\Delta H(\text{ECW})$, between *tert*-butyl alcohol (donor) and the solvent (acceptor), *t*-BuOH- -S. According to the interpretation of Wayner et al.,² this enthalpy can in turn be identified with the difference $\Delta_{\text{sln}} H^\circ(t\text{-BuOH}, \text{g}) - \Delta_{\text{sln}} H^\circ(t\text{-BuO}^\bullet, \text{g})$, allowing the evaluation of $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H})$ from eq 10.

Unfortunately, the ECW parameters for toluene, ethylbenzene, and cumene are not available. However, it seems sensible to use the ECW values corresponding to benzene, since the strength and nature of the intermolecular interactions are similar in benzene and toluene,³² and this should be even more so for the remaining two alkylbenzenes. This assumption can be further substantiated by noting that, according to an alternative procedure to estimate solvation terms,^{4,33,34} the parameters are the same for both benzene and toluene. On this basis, one obtains

$\Delta H(\text{ECW}) = -4.4 \pm 1 \text{ kJ mol}^{-1}$,⁴ and therefore $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H}) = 454.3 \pm 3.1 \text{ kJ mol}^{-1}$.

The second approach to evaluate $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H})$ uses the solution phase O-O bond dissociation enthalpy in di-*tert*-butylperoxide, $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{OBu-}t)$, as the starting point. In a previous work,⁴ we have reported this enthalpy in several solvents, including benzene, through a static PAC study of reaction 5 alone. The enthalpy of this reaction, $\Delta_r H_1$, is equal to $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{OBu-}t)$. The relation between both bond dissociation enthalpies is given by eq 12.

$$\begin{aligned} DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H}) &= \Delta_r H^\circ(t\text{-BuO}^\bullet, \text{sln}) + \Delta_r H^\circ(\text{H}^\bullet, \text{sln}) - \Delta_r H^\circ(t\text{-BuOH}, \text{sln}) \\ &= DH_{\text{sln}}^\circ(t\text{-BuO} - \text{OBu-}t) / 2 + [\Delta_r H^\circ(t\text{-BuOOBu-}t, \text{l}) + \Delta_{\text{sln}} H^\circ(t\text{-BuOOBu-}t, \text{l})] / 2 + \Delta_r H^\circ(\text{H}^\bullet, \text{g}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) - \Delta_r H^\circ(t\text{-BuOH}, \text{l}) - \Delta_{\text{sln}} H^\circ(t\text{-BuOH}, \text{l}) \quad (12) \end{aligned}$$

The solution quantities in eq 12 should be very similar in benzene and in the alkylbenzene solutions used in the present work. Therefore, the required values to obtain $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H})$ are the O-O bond dissociation enthalpy of di-*tert*-butylperoxide in benzene ($156.7 \pm 9.9 \text{ kJ mol}^{-1}$), determined by PAC, together with the solution enthalpies of di-*tert*-butylperoxide ($1.21 \pm 0.22 \text{ kJ mol}^{-1}$) and *tert*-butyl alcohol ($15.5 \pm 0.4 \text{ kJ mol}^{-1}$) in benzene, both determined using reaction-solution calorimetry.⁴ The remaining auxiliary values are the enthalpies of formation of di-*tert*-butylperoxide, *tert*-butyl alcohol, and the hydrogen atom.^{35,36} Finally, using the same estimate for the solvation enthalpy of the hydrogen atom as above, one obtains $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H}) = 455.2 \pm 5.2 \text{ kJ mol}^{-1}$. This result is very close to the one obtained from the ECW procedure, but has the advantage of relying on a value directly measured in solution.

The previous methodologies illustrate how $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{OBu-}t)$ can be used to derive $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{H})$, which in turn affords $DH_{\text{sln}}^\circ(\text{C} - \text{H})$ through eq 9. However, recall that TR-PAC can provide the enthalpy of *both* processes in Scheme 1, i.e., reactions 5 and 6. Therefore, by combining eqs 9 and 12, we can derive eq 13, where $\Delta_r H_1$ and $\Delta_r H_2$ are the enthalpies of reaction 5 and 6, respectively, determined in the *same* TR-PAC experiment.

$$\begin{aligned} DH_{\text{sln}}^\circ(\text{C} - \text{H}) &= (\Delta_r H_1 + \Delta_r H_2) / 2 + [\Delta_r H^\circ(t\text{-BuOOBu-}t, \text{l}) + \Delta_{\text{sln}} H^\circ(t\text{-BuOOBu-}t, \text{l})] / 2 + \Delta_r H^\circ(\text{H}^\bullet, \text{g}) + \Delta_{\text{sln}} H^\circ(\text{H}^\bullet, \text{g}) - \Delta_r H^\circ(t\text{-BuOH}, \text{l}) - \Delta_{\text{sln}} H^\circ(t\text{-BuOH}, \text{l}) \quad (13) \end{aligned}$$

In other words, this third procedure has the advantage that all the solution terms can be determined (with the exception of the solvation enthalpy of the hydrogen atom) in the same mixtures used in the experiment, i.e., we do not need to assume that $DH_{\text{sln}}^\circ(t\text{-BuO} - \text{OBu-}t)$ is identical in benzene and in the experimental solutions (see, however, below). Therefore, using eq 13, together with the solution enthalpies of di-*tert*-butylperoxide ($-0.47 \pm 0.72 \text{ kJ mol}^{-1}$) and *tert*-butyl alcohol ($15.2 \pm 0.6 \text{ kJ mol}^{-1}$) in toluene, measured by reaction-solution calorimetry, the only remaining assumption regards the hydrogen atom solvation enthalpy.³⁷

Before summing up the final results and deciding on the best of the above three procedures, it is appropriate to review and analyze in more detail the assumptions involved in each of them. The results obtained for the C–H bond dissociation enthalpy in toluene $DH_{\text{sln}}^{\circ}(\text{C} - \text{H})$ are (in kJ mol⁻¹): 374.4 ± 3.7 , 375.3 ± 5.6 , and 380.5 ± 5.1 , using the three procedures in the order presented above. The first two values are almost identical, reflecting the similarity between $DH_{\text{sln}}^{\circ}(t\text{-BuO} - \text{H})$ from the corresponding procedures. Recall that the first one is derived from the gas-phase result with the (small) ECW correction, while the second relies on the experimental PAC measurement of $DH_{\text{sln}}^{\circ}(t\text{-BuO} - \text{O}Bu\text{-}t)$, and therefore requires the volume correction for reaction 5 when evaluating $\Delta_r H_1$ through eq 2. The similarity of the results supports this correction (with $\Delta_r V_1 = 13.4 \text{ mL mol}^{-1}$).² However, both values still refer to solvation in benzene, while the experimental solutions include the other alkylbenzenes.

The fact that the $DH_{\text{sln}}^{\circ}(\text{C} - \text{H})$ result from eq 13 (using data obtained in toluene) is in good agreement with the values derived from the first and second methods confirms the similarities in the solvation energetics of benzene and toluene. This agreement also supports other hypotheses used above, viz. the volume change correction and the validity of the correlation used to estimate the quantum yield.²⁷ Nevertheless, since the third procedure is less dependent on assumptions, we decided to adopt its result for toluene. On the other hand, as the differences in $DH_{\text{sln}}^{\circ}(\text{C} - \text{H})$ are small (ca. 5 kJ mol⁻¹), for the remaining alkylbenzenes we opted for the second procedure, which is experimentally less demanding.³⁸ There is, however, a better way of dealing with the C–H bond dissociation enthalpies in these compounds (see below). Table 1 displays the results of the above calculations leading to the values of $DH_{\text{sln}}^{\circ}(\text{C} - \text{H})$ for toluene, ethylbenzene, and cumene.

A final word of caution concerning the third procedure: in some experiments, the substrate may also absorb considerably at the excitation wavelength, interfering with the measured photoacoustic signal of the photochemically active substance (di-*tert*-butylperoxide). In those cases, TR–PAC analysis will not reveal the correct enthalpy of reaction 5 (Scheme 1). However, this contribution resulting from the substrate absorption may only affect the measured amplitude of the first process, but not of the second, which is much slower.⁵ Therefore, the amplitude of the second process, obtained from the deconvolution, is still exclusively related to reaction 6, allowing the correct calculation of the bond dissociation enthalpy using either the first or the second procedure above.³⁹

Each gas-phase bond dissociation enthalpy for the alkylbenzenes is related to the solution result by eq 14.

$$DH^{\circ}(\text{C} - \text{H}) = DH_{\text{sln}}^{\circ}(\text{C} - \text{H}) + \Delta_{\text{sln}} H^{\circ}(\text{PhRH}, \text{g}) - \Delta_{\text{sln}} H^{\circ}(\text{PhR}^{\bullet}, \text{g}) - \Delta_{\text{sln}} H^{\circ}(\text{H}^{\bullet}, \text{g}) \quad (14)$$

This equation shows that the hydrogen atom solvation enthalpy cancels out when the gas-phase value is calculated from the solution value (e.g., combine eqs 13 and 14). Yet, the differential solvation between the alkylbenzene compound and its radical needs to be considered. Contrasting with the above example for *t*-BuOH (and also for other hydrogen donor compounds such as phenols² and, to a lesser extent, thiophenols⁵), Kanabus-Kaminska et al. suggested that alkyl radicals (R^{\bullet}) and their corresponding precursors (RH) have similar solvation enthalpies.³ This implies that $\Delta_{\text{sln}} H^{\circ}(\text{PhRH}, \text{g}) - \Delta_{\text{sln}} H^{\circ}(\text{PhR}^{\bullet}, \text{g})$ in eq 14 is close to zero.

Our results for the gas-phase C–H bond dissociation enthalpies and the corresponding standard enthalpies of formation of

TABLE 1: C–H Bond Dissociation Enthalpies in Solution, $DH_{\text{sln}}^{\circ}(\text{C} - \text{H})$, Determined by TR–PAC, for Toluene, Ethylbenzene, and Cumene (data in kJ mol⁻¹)

substrate	$\Delta_{\text{obs}} H_2^a$	Φ_r^b	$\Delta_r H_2^c$	$DH_{\text{sln}}^{\circ}(\text{C} - \text{H})$
PhCH ₃	132.7 ± 3.5	0.83	-159.9 ± 4.2	380.5 ± 5.1^d
PhCH ₂ CH ₃	149.9 ± 1.3	0.82	-182.8 ± 1.6	363.8 ± 5.3^e
PhCH(CH ₃) ₂	153.9 ± 2.5	0.81	-190.0 ± 3.1	360.2 ± 5.4^e

^a Measured enthalpy change for the sequential slower process, attributed to reaction 6 (average of five experiments; the error is twice the standard deviation of the mean in each case). ^b The *t*-BuO–O*Bu*-*t* homolysis quantum yield in the respective solution was estimated from a correlation described in ref 2 (see also note 27). ^c Enthalpy of reaction 6, calculated with eq 8. ^d Calculated from eq 13 with $\Delta_r H_1 = 168.3 \pm 8.8 \text{ kJ mol}^{-1}$. ^e Calculated using $DH_{\text{sln}}^{\circ}(t\text{-BuO} - \text{H}) = 455.2 \pm 5.2 \text{ kJ mol}^{-1}$ in eq 9.

TABLE 2: Gas-Phase C–H Bond Dissociation Enthalpies and Standard Enthalpies of Formation of Alkylbenzyl Radicals (data in kJ mol⁻¹)

radical	$DH^{\circ}(\text{C} - \text{H})$	$\Delta_f H^{\circ}(\text{PhRH}, \text{g})^a$	$\Delta_f H^{\circ}(\text{PhR}^{\bullet}, \text{g})^b$
PhCH ₂ •	375.5 ± 5.0	50.5 ± 0.5	208.0 ± 5.0
PhCH•CH ₃	358.8 ± 5.2	30.0 ± 1.0	170.8 ± 5.3
PhC•(CH ₃) ₂	355.2 ± 5.3	4.0 ± 1.0	141.2 ± 5.4

^a Values from ref 35. ^b $\Delta_f H^{\circ}(\text{PhR}^{\bullet}, \text{g}) = DH^{\circ}(\text{C} - \text{H}) + \Delta_f H^{\circ}(\text{PhRH}, \text{g}) - \Delta_f H^{\circ}(\text{H}^{\bullet}, \text{g})$.

the alkylbenzyl radicals (derived using the standard enthalpies of formation of the corresponding alkylbenzenes and the hydrogen atom)^{35,36} are summarized in Table 2.

The touchstone for discussing the results in Table 2 is the enthalpy of formation of the benzyl radical. Table 3 lists a collection of literature values for this quantity (and the corresponding gas-phase bond dissociation enthalpies) reported over the past 20 years.^{10,11,40–43} Also included in the table are results derived from a gas-phase acidity cycle⁴⁴ (eq 15) and a proton affinity cycle⁴⁵ (eq 16), using the most recent data from the NIST Chemistry WebBook.¹⁴

$$DH^{\circ}(\text{PhCH}_2 - \text{H}) = \Delta_{\text{acid}} H + EA(\text{PhCH}_2^{\bullet}) - IE(\text{H}^{\bullet}) \quad (15)$$

$$DH^{\circ}(\text{PhCH}_2 - \text{H}) = PA(\text{PhCH}_2^{\bullet}) + IE(\text{PhCH}_3) - IE(\text{H}^{\bullet}) \quad (16)$$

The values in Table 3 that appeared before Tsang's review were discussed by this author, who recommended $\Delta_f H^{\circ}(\text{PhCH}_2^{\bullet}, \text{g}) = 207 \pm 5 \text{ kJ mol}^{-1}$.¹⁰ They reflect a considerable improvement on the dispersion of older results. The first determination of the enthalpy of formation of PhCH₂• (155 kJ mol⁻¹), made by Szwarc ca. 50 years ago,⁴⁶ is 45 kJ mol⁻¹ lower than the value recommended by McMillen and Golden ($200 \pm 6 \text{ kJ mol}^{-1}$).⁴⁰ The modern results obtained from kinetic studies in the gas phase (shock tubes) are considered to be quite reliable. As pointed out by Tsang,¹⁰ their accuracy depends, however, on the uncertainty of the temperature correction to 298.15 K. Nevertheless, it is noted that the most recent gas-phase kinetics value, $210 \pm 5 \text{ kJ mol}^{-1}$, is in very good agreement with Tsang's selection. This new value was obtained from shock-tube (ST) experiments in conjunction with early very low pressure pyrolysis (VLPP) data.¹¹ These calculations were required because the ST experimental conditions were in the falloff regime, but this strategy is claimed to provide a more accurate value than ST results alone.

As mentioned above, it is also possible to derive the enthalpy of formation of the benzyl radical through a gas-phase acidity cycle or a proton affinity cycle with the required auxiliary data

TABLE 3: Values of the Standard Enthalpy of Formation of the Benzyl Radical and the Corresponding Gas-Phase PhCH₂–H Bond Dissociation Enthalpy at 298.15 K (data in kJ mol⁻¹)

authors (year)	method ^a	$DH^\circ(\text{PhCH}_2\text{--H})$	$\Delta_f H^\circ(\text{PhCH}_2^\bullet, \text{g})$	ref
McMillen and Golden (1982)	review ^b	368 ± 6 ^c	200 ± 6	40
Hippler and Troe (1990)	ST	378 ± 4 ^c	210.5 ± 4	41
Walker and Tsang (1990)	ST	371 ± 6 ^c	203 ± 6	42
Tsang (1996)	review ^d	375 ± 5 ^c	207 ± 5	10
Ellison et al. (1996)	GPA (FA)	375.7 ± 2.5	208.2 ± 2.5 ^c	43
NIST Database (2003)	GPA ^e	363 ± 9	195 ± 9 ^c	14
NIST Database (2003)	GPA ^f	369 ± 9	201 ± 9 ^c	14
NIST Database (2003)	PA	371 ± 8	203 ± 8 ^c	14
Song et al. (2002)	ST/VLPP	378 ± 5 ^c	210 ± 5	11
this work	TR–PAC	375.5 ± 5.2	208.0 ± 5.2	this work

^a FA = flowing afterglow; GPA = gas-phase acidity cycle; PA = proton affinity cycle; ST = shock tubes; TR–PAC = time-resolved photoacoustic calorimetry; VLPP = very low pressure pyrolysis. ^b The recommended enthalpy of formation relies on kinetic data obtained by the iodination technique. ^c Recalculated with $\Delta_f H^\circ(\text{PhCH}_3, \text{g}) = 50.5 \pm 0.5$ kJ mol⁻¹ (ref 35). ^d Average between the two previous ST results, as stated in ref 10. ^e Based on data from Gal, J. F.; Decouzon, M.; Maria, P. C.; Gonzalez, A. I.; Mo, O.; Yanez, M.; El Chaouch, S.; Guillemin, J. C. *J. Am. Chem. Soc.* **2001**, 123, 6353. ^f Based on data from Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, 101, 6047.

from the NIST Chemistry WebBook.¹⁴ Both results are in good agreement with selected gas-phase kinetics values, but this agreement is due to higher uncertainty intervals. A more accurate value (208.2 ± 2.5 kJ mol⁻¹), also based on an acidity cycle, is shown in Table 3. Ellison et al.⁴³ used flowing afterglow/selected ion flow tube (FA/SIFT) experiments to measure the direct and inverse rates of suitable equilibrium reactions at 300 K, whose ratio provided the acidity of toluene, tied to the firmly established acidity of methanol. The associated entropy change was calculated using equilibrium statistical mechanics. With this procedure the authors claim an overall accuracy of 3 kJ mol⁻¹ or better.

The value recommended by Tsang and those reported by Ellison et al. and Song et al. fall in a rather narrow range and are very close to the result from a very recent quantum chemistry study. Henry et al.⁴⁷ used a selection of the most accurate high level computational procedures (as tested against accurately known experimental enthalpies of formation of a number of organic radicals) to predict $\Delta_f H^\circ$ values for several species, including benzyl radical. The value selected from the “best performing” methods (W1h, G3-RAD, G3X-RAD), corrected to 298.15 K,¹¹ is 207 ± 4 kJ mol⁻¹. As observed in Table 3, the solution-based TR–PAC value derived in the present study is in excellent agreement with the “best” available data.

The discussion can now be extended to the remaining alkylbenzenes. The hydrogen abstraction reaction illustrated in Scheme 1 occurs, for all alkylbenzenes, at the C1 carbon of the alkyl group. The alkylbenzyl radical thus generated is stabilized by the combined effect of resonance from the aromatic ring and hyperconjugation from the remaining alkyl groups. This stabilization increases as the hydrogen abstracted changes from a primary carbon in toluene to a secondary carbon in ethylbenzene and finally to a tertiary carbon in cumene, with a concomitant decrease in $DH^\circ(\text{C–H})$. This effect can be more conveniently illustrated using a *relative* scale of bond dissociation enthalpies, $\Delta DH^\circ(\text{C–H})$, which expresses the change in bond dissociation enthalpy for the alkylbenzene (PhRH) relative to toluene itself (eq 17).

$$\Delta DH^\circ(\text{C–H}) = DH^\circ(\text{PhR–H}) - DH^\circ(\text{PhCH}_2\text{–H}) \quad (17)$$

Positive and negative values of $\Delta DH^\circ(\text{C–H})$ imply either a strengthening or a weakening of the bond, respectively, relative to the C–H bond in toluene. The relative scales in the gas-phase, $\Delta DH^\circ(\text{C–H})$, and in solution, $\Delta DH^\circ_{\text{sln}}(\text{C–H})$, are

related by eq 18:

$$\begin{aligned} \Delta DH^\circ(\text{C–H}) = & \Delta DH^\circ_{\text{sln}}(\text{C–H}) + [\Delta_{\text{sln}} H^\circ(\text{PhRH}, \text{g}) - \\ & \Delta_{\text{sln}} H^\circ(\text{PhR}^\bullet, \text{g})] - [\Delta_{\text{sln}} H^\circ(\text{PhCH}_3, \text{g}) - \\ & \Delta_{\text{sln}} H^\circ(\text{PhCH}_2^\bullet, \text{g})] \quad (18) \end{aligned}$$

An important advantage of using the relative scale defined by eq 17 is that the hypothesis of cancellation of the solvation terms, $\Delta_{\text{sln}} H^\circ(\text{PhRH}, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{PhR}^\bullet, \text{g})$, required to derive the gas-phase from the solution-phase bond dissociation enthalpies (eq 14), is now replaced by an even more reliable assumption: $\Delta_{\text{sln}} H^\circ(\text{PhRH}, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{PhR}^\bullet, \text{g}) \approx \Delta_{\text{sln}} H^\circ(\text{PhCH}_3, \text{g}) - \Delta_{\text{sln}} H^\circ(\text{PhCH}_2^\bullet, \text{g})$. In addition, the use of eq 18 eliminates the need of the enthalpy of solvation of the hydrogen atom. Therefore, $\Delta DH^\circ(\text{C–H}) \approx \Delta DH^\circ_{\text{sln}}(\text{C–H})$, i.e., the relative scale will be identical in solution and in the gas-phase.

The relative values are also much more readily calculated from the experimental TR–PAC results than the absolute data presented in Tables 1 and 2. Applying eqs 9 and 17 to toluene and to another alkylbenzene, eq 19 is obtained, where $\Delta_f H_2$ and $\Delta_f H'_2$ are the enthalpies of reaction 6 for PhRH and for PhCH₃, respectively.

$$\Delta DH^\circ(\text{C–H}) \approx \Delta DH^\circ_{\text{sln}}(\text{C–H}) = \Delta_f H_2/2 - \Delta_f H'_2/2 \quad (19)$$

This equation presents several further advantages. Recall that the volume change correction of reaction 5 is not needed to evaluate the reaction enthalpies in eq 19. Moreover, it also avoids the assumption $\Delta_f V_2 \approx 0$. Also, the uncertainties affecting the values of $\Delta DH^\circ(\text{C–H})$ are *smaller* than the uncertainties assigned to the respective absolute values, since no auxiliary data are needed.⁴⁸ Finally, the use of relative values allows a better comparison with literature data.

To the best of our knowledge, the only complete studies leading to the enthalpies of formation of alkylbenzyl radicals and the corresponding C–H bond dissociation enthalpies are those by Robaugh and Stein¹² and by Mautner.¹³ The first of these works describes a VLPP study of the thermal unimolecular decomposition of ethylbenzene, isopropylbenzene, and *tert*-butylbenzene, yielding methyl radical and the corresponding alkylbenzyl radical. From the enthalpies of these reactions, Robaugh and Stein derived the enthalpies of formation of the ethylbenzyl and cumyl radicals (the enthalpy of formation of the benzyl radical was taken as 196.6 kJ mol⁻¹).⁴⁹ These values can now be used to calculate the C–H bond dissociation

TABLE 4: Gas-Phase C–H Bond Dissociation Enthalpies for Ethylbenzene and Cumene Relative to Toluene, $\Delta DH^\circ(\text{C} - \text{H})$ (data in kJ mol⁻¹)

authors (year)	method ^a	PhCH ₂ CH ₃	PhCH(CH ₃) ₂
Robaugh and Stein (1981)	VLPP	-10	-15
Mautner (1982)	ICR(PA)	-11.3	-11.7
McMillen and Golden (1982)	review	-10.9	-15.1
NIST Database (2003)	PA	-0.5	1.3
this work	TR-PAC	-11.5 ± 2.2 ^b	-15.1 ± 2.6 ^b

^a ICR = ion cyclotron resonance mass spectrometry; PA = proton affinity cycle; TR-PAC = time-resolved photoacoustic calorimetry; VLPP = very low pressure pyrolysis. ^b Values calculated with eq 19.

enthalpies of ethylbenzene and cumene relative to the C–H bond dissociation enthalpy in toluene, by using the standard enthalpies of formation of the parent alkylbenzenes (Table 2). The values of $\Delta DH^\circ(\text{C} - \text{H})$ thus calculated are displayed in Table 4.

In the second work mentioned, Mautner used ion cyclotron resonance mass spectrometry (ICR) and bracketing reactions to determine the proton affinities (PA) of several alkylbenzyl radicals relative to the PA of benzyl radical, which was obtained from a proton affinity cycle (eq 16) with $DH^\circ(\text{PhCH}_2 - \text{H}) = 372.0 \text{ kJ mol}^{-1}$.¹³ Using the same cycle, Mautner then derived $DH^\circ(\text{C} - \text{H})$ for several compounds, including ethylbenzene and cumene. The $\Delta DH^\circ(\text{C} - \text{H})$ values displayed in Table 4 were calculated with eq 20.

$$\Delta DH^\circ(\text{C} - \text{H}) = [PA(\text{PhR}^\bullet) - PA(\text{PhCH}_2^\bullet)] + [IE(\text{PhRH}) - IE(\text{PhCH}_3)] \quad (20)$$

This equation can also be used to calculate $\Delta DH^\circ(\text{C} - \text{H})$ values from proton affinity and adiabatic ionization energy data recommended in the NIST Chemistry WebBook.^{14,50}

In principle, $\Delta DH^\circ(\text{C} - \text{H})$ values could also be derived from gas-phase acidity cycles (eq 21), using data from the NIST Chemistry WebBook.¹⁴ However, although the acidities of ethylbenzene and cumene are available, the electron affinities of the corresponding radicals were derived from those acidity data and the C–H bond dissociation enthalpies.¹⁴ Therefore, the comparison is redundant.

$$\Delta DH^\circ(\text{C} - \text{H}) = [\Delta_{\text{acid}} H(\text{PhRH}) - \Delta_{\text{acid}} H(\text{PhCH}_3)] + [EA(\text{PhR}^\bullet) - EA(\text{PhCH}_2^\bullet)] \quad (21)$$

It is observed (Table 4) that the TR-PAC relative C–H bond dissociation enthalpies are in close agreement with the values reported by Robaugh and Stein,¹² by Mautner,¹³ and with those recommended in McMillen and Golden's review.⁴⁰ The trend seems, therefore, quite well established: the primary C–H bond dissociation enthalpy in toluene is about 11 kJ mol⁻¹ higher than the secondary C–H bond in ethylbenzene, and 15 kJ mol⁻¹ higher than the tertiary C–H bond in cumene. This trend can be compared, for example, with the one observed in alkyl radicals, where the C–H bond dissociation enthalpy in ethane is 9 kJ mol⁻¹ higher than the secondary C–H bond in propane and 21 kJ mol⁻¹ higher than the tertiary C–H bond in 2-methylpropane.^{10,35,36}

The relative values derived from the proton affinity cycle and data recommended in the NIST Chemistry WebBook,¹⁴ which indicate that there is almost no variation in the C–H bond dissociation enthalpies, are not in keeping with the remaining results in Table 4.

Conclusions

Like all gas-phase techniques mentioned in the above discussion, photoacoustic calorimetry also has its virtues and

its problems. The disadvantages attributed to PAC (based on the strategy presented in Scheme 1) have been mainly the need for a volume change correction and, as with any other solution technique, the proper accounting for the solvation effects (if one is interested in deriving gas-phase values). However, the former is no longer a serious problem when the number of reactant molecules is equal to the number of product molecules in the reaction of interest and the energetics of this reaction can be probed by TR-PAC. With regard to the solvation corrections, the excellent agreement between the TR-PAC values and the "best" gas-phase results in Tables 3 and 4 support the methods used and assumptions made, in particular that the solvation enthalpies of the alkylbenzyl radicals and the respective alkylbenzene compounds are similar. This conclusion, however, must be taken with caution, since there is evidence that other systems require a careful assessment of the differential solvation of the substrate and its radical.⁵¹

Given the number of independent experimental results that are now available for the enthalpy of formation of benzyl radical, confirmed by high-level theoretical calculations, the excellent agreement with the TR-PAC value determined in the present study is another valid test of this technique as a tool for obtaining high quality thermochemical data for radical species. The obtained relative values for C–H bond dissociation enthalpies in ethylbenzene and cumene, corroborating expected trends, further support that claim and illustrate the general applicability of the technique.

Acknowledgment. We thank Dr. Manuel Minas da Piedade (FCUL) and Dr. Hermínio Diogo (Instituto Superior Técnico; Lisboa) for assistance with the reaction-solution calorimetry experiments. This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal (POCTI/35406/QUI/1999). V. S. F. M. thanks FCT for a PhD grant (SFRH/BD/2828/2000).

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- (26) Toluene was thus used as pure solvent. For the remaining alkylbenzenes, solutions in benzene were prepared with the following concentrations: 4.1 M of ethylbenzene, and 1.5 to 3.6 M of cumene. Benzene was used in these cases as a kinetic buffer: by lowering the concentration of the substrate one can adjust the lifetime of the second process (the rate of reaction 6, see Scheme 1). This is important because the accuracy of the deconvolution is dependent on achieving a good temporal separation between the processes involved (ref 21), which may require the tuning of the lifetime of the second process.
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- (38) There is an additional problem if the third procedure is to be used when the experimental solution is a mixture. The experiments in toluene were made in the neat solvent, so the expansion coefficient is simply that of the pure substance, $\chi = 0.7250 \text{ mL kJ}^{-1}$ (calculated with data from Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; Wiley: New York, 1986). However, given the high concentrations used for the remaining alkylbenzenes (see note 26), a weighted average of the solvent and solute expansion coefficients should be used. Fortunately, considering the similarity of the molecules involved (benzene, toluene, ethylbenzene, and cumene), the changes in the expansion coefficient are relatively small. Furthermore, the weight of the volume correction on the final result is minimal. For the molecules studied, the maximum difference in the expansion coefficients exists between ethylbenzene ($0.6775 \text{ mL kJ}^{-1}$) and benzene ($0.7989 \text{ mL kJ}^{-1}$), which amounts to a change in the final result of only ca. 1.5 kJ mol^{-1} , using the third procedure.
- (39) As indicated before (see note 23), the subtraction of the solvent waveform can minimize the contribution of the background signal. We verified that this practice provided an improvement in the accuracy of the determination of $\Delta_r H_1$ (while not significantly affecting $\Delta_r H_2$), because it leads to $DH_{\text{sin}}^\circ(t\text{-BuO} - \text{OBu-}t)$ values in much better agreement with the ones obtained from independent classical PAC experiments (ref 4).
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- (45) The required auxiliary data are the proton affinity of the benzyl radical, $PA(\text{PhCH}_2^\bullet) = 831.4 \pm 8 \text{ kJ mol}^{-1}$, and the adiabatic ionization energies of toluene $IE(\text{PhCH}_3) = 851.77 \pm 0.10 \text{ kJ mol}^{-1}$, and of the hydrogen atom (as in note 44; data from ref 14).
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- (48) Note that we are assuming that the $DH_{\text{sin}}^\circ(t\text{-BuO} - \text{H})$ value is identical in all the experimental solutions. This assumption is, however, supported by the discussion concerning the results in Table 1.
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- (50) The required auxiliary data are: the proton affinities of the benzyl radical (see note 45) and the alkylbenzyl radicals, $PA(\text{PhCH}^\bullet\text{CH}_3) = 836.5 \pm 8 \text{ kJ mol}^{-1}$ and $PA(\text{PhC}^\bullet(\text{CH}_3)_2) = 842.2 \pm 8 \text{ kJ mol}^{-1}$; the adiabatic ionization energies of toluene (note 45) and the alkylbenzenes, $IE(\text{PhCH}_2\text{-CH}_3) = 846.2 \pm 1.0 \text{ kJ mol}^{-1}$ and $IE(\text{PhCH}(\text{CH}_3)_2) = 842.3 \pm 1.9 \text{ kJ mol}^{-1}$ (data from ref 14).
- (51) Guedes, R. C.; Coutinho, K.; Cabral, B. J. C.; Canuto, S.; Correia, C. F.; Borges dos Santos, R. M.; Martinho Simões, J. A. *J. Phys. Chem. A*, **2003**, *107*, 9197.