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Determination of Bond Dissociation Enthalpies in Solution by Photoacoustic Calorimetry

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Introduction

The enthalpy change that occurs in a photoinduced chemical reaction in solution can be quantified by a relatively simple technique known as photoacoustic calorimetry (PAC), which allows measurements to be performed under conditions (i.e., temperature, solvent, etc.) relevant to most chemical and biochemical processes. Photoacoustic calorimetry was first applied in 1983 to radical processes by Rothberg et al.,[1] who determined the enthalpy of hydrogen abstraction from aniline by triplet benzophenone to form the benzhydrol amine radical pair. Peters and co-workers[2] developed a time-resolved method to deconvolute the photoacoustic signal from the sample solution into a detector response function (obtained from calibration) and a (time-dependent) response from the process under study. At about the same time, Griller and co-workers[3] focused on the application of PAC to the determination of bond dissociation enthalpies (BDEs), using an instrument adapted from that used by Peters, but with the experimental method similar to that described in this Account.

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Bond strengths and heats of formation, $\Delta_f H$, are of great importance in understanding the stability and reactivity of reactive species, such as radicals. In most cases, consideration of the enthalpy allows one to predict the course (selectivity) of a reaction. While the bond strengths in many simple hydrocarbons have been measured using various gas phase techniques[4] to a precision of 1−2 kcal mol^{-1}, the accepted absolute values have changed significantly over the last 30 years. For instance, the BDE(C−H) in benzene has risen from 103[5] to 113.5[6] kcal mol^{-1} and that of the benzylic C−H in toluene from 85[5] to 90[4] kcal mol^{-1}. Consequently, many BDEs that were derived using these reference values changed as well. Despite their importance, BDEs in more complex species are more difficult to measure and thus less reliable.[7] Experimental approaches for the direct and indirect determination of BDEs in the gas phase[4,7] or in solution (electrochemical cycles[8] and PAC) as well as new computational methods such as density functional theory[9] have led to a dramatic increase in the number of reliable BDEs for organic and organometallic compounds. For consistency, all of the data are normally extrapolated to standard state conditions (i.e., 298 K in the gas phase). While this extrapolation allows for comparison with the vast store of gas phase data, some questions have emerged concerning solvent effects on the reaction and bond dissociation enthalpies. For practical purposes, most chemical processes of interest to chemists and biochemists occur in the condensed phase (usually in solution) and therefore direct measurement of solution thermodynamics precludes the need to assess the effect of the solvent.

This Account describes the recent advances in the application of PAC for the determination of bond dissociation enthalpies (eqs 1 and 2). Although the experimental approach is relatively straightforward, the proper treatment of the data requires detailed insight into the fundamental aspects of the technique. Without these considerations, large systematic errors and thus erroneous results may arise. In the recent period, we have developed a detailed methodology to ensure that the PAC enthalpy determinations are consistent and that solvent effects are correctly incorporated.

$$\mathrm{R{-}H} \rightarrow \mathrm{R^{\bullet}} + \mathrm{H^{\bullet}} \quad (1)$$

$$\mathrm{BDE(R{-}H)} = \Delta_f H(\mathrm{R^{\bullet}}) + \Delta_f H(\mathrm{H^{\bullet}}) - \Delta_f H(\mathrm{RH}) \quad (2)$$

The Photoacoustic Response

Photoacoustic calorimetry is a thermodynamic method to determine a bond strength in solution. The physical basis for PAC is deceptively simple; rapid heat release from a photoinitiated process in a limited, well-defined volume results in a local change in density, generating a pressure wave that propagates through the solution at the speed of sound. Detection and quantification of this pressure wave is the basis of the technique.

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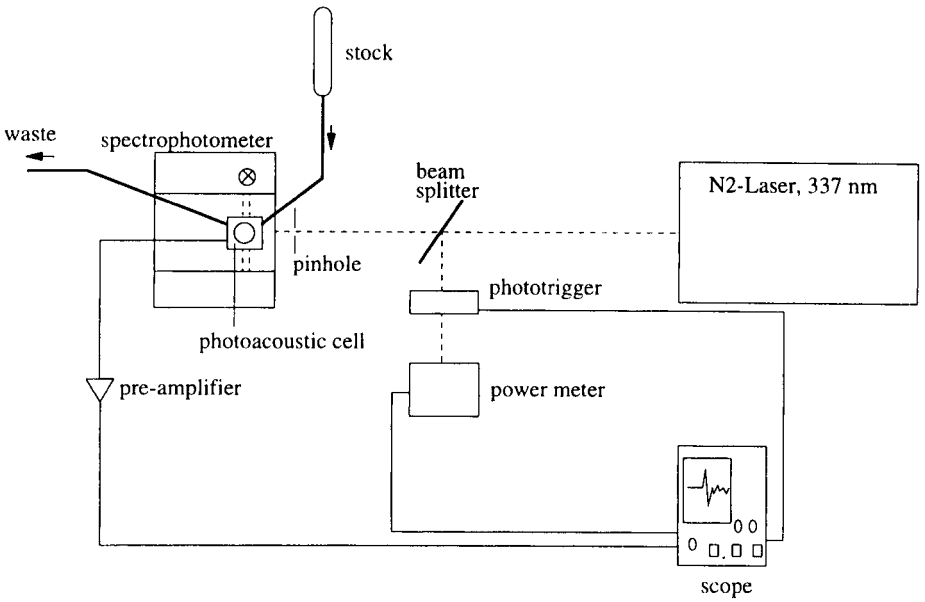


FIGURE 1. Block diagram of the PAC instrument. The laser pulse passes through a beam splitter which sends a small fraction (ca. 10%) of the incident light to a phototrigger and power meter to normalize for laser energy fluctuations. The remaining light initiates the photoreaction in the photoacoustic cell. The transmission of the sample is measured with a spectrophotometer (the spectrophotometer can be replaced with a second power meter). Solutions are allowed to flow slowly through the cell to ensure that reagents are not depleted. The signals are amplified and collected by a digital oscilloscope and analyzed using a PC.

With PAC, only the heat released within a well-defined time interval is detected (prompt heat release; vide infra). The heat integration time is determined by the properties of the instrument and the detector. Density changes due to gradual heat dissipation do not contribute measurably to the photoacoustic response. Thus, the time dependence can be used to advantage since it is possible to discriminate against "slow" processes such as relaxation from a triplet state or reactions at or above the millisecond time scale.

The relation between the heat release and the photoacoustic response has been described mathematically by adapting basic equations from fluid mechanics to the experimental circumstances in PAC.[1,10−14] While several reports have appeared over the last two decades, in which the development and applications of PAC are described,[15−19] in this Account we will highlight the procedure by which reaction enthalpies are retrieved from a photoacoustic experiment. The photoacoustic effect is a consequence of nonradiative deactivation by internal conversion, intersystem crossing, or a chemical reaction of an excited state formed after absorbing the photon energy, $E_{h\nu}$. Equation 3 provides the relation between the

$$E_{\mathrm{th}} = f_{\mathrm{th}} E_{h\nu}(1 - 10^{-A}) \tag{3}$$

fraction of absorbed light, $f_{\mathrm{th}}E_{h\nu}(1 - 10^{-A})$ with A as the absorbance, and the thermal energy, E_{th}. The resulting temperature increase in the irradiated cylindrical volume as determined by the heat capacity of the solution, C_p, causes the medium to expand. The magnitude of the expansion is related to the isobaric expansion coefficient of the solvent, α. If the thermal expansion is adiabatic (i.e., no heat diffusion occurs), the increase in volume is proportional to the amount of released heat. The volume change initiates a thermal shock, which is detected as a pressure change by a piezoelectric sensor (microphone). The magnitude of the observed pressure change is linearly proportional to the displacement and thus to the initial heat release.

The observed pressure wave is a measure of the total volume expansion that has occurred: a composite of expansion due to the release of chemical heat and that due to the change in the volume occupied by the products compared to reactants ($\Delta_r V$).[20] The former is the desired quantity for calculating of the reaction enthalpy. The latter quantity, the reaction volume change, is only significant when the number of chemical species changes (i.e., when the number of bonds broken is not equal to the number of bonds formed) or when large conformational changes occur in more complex molecules, such as proteins.[20−22] The detector cannot discriminate between these two volume changes. The experimentally observed photoacoustic response, S_{obs}, is described by eq 4, in which c is

$$S_{\mathrm{obs}} = c f_{\mathrm{obs}} E_{h\nu} \chi_{\mathrm{s}} (1 - 10^{-A}) \tag{4}$$

an instrumental response factor, f_{obs} is the apparent fraction of light converted into heat (vide infra), and χ_{s} is the adiabatic expansion coefficient of the medium which equals $M\alpha/C_p\rho$, where M is the molecular weight and ρ the density. Therefore, it is necessary to extract the value of f_{th} from the experimentally determined f_{obs}. We define the magnitude of S_{obs} as the peak-to-peak amplitude of the first oscillation. A simple block diagram of the instrument is shown in Figure 1. A typical transducer response generated by a photoacoustic shock wave is shown in the inset of Figure 2.

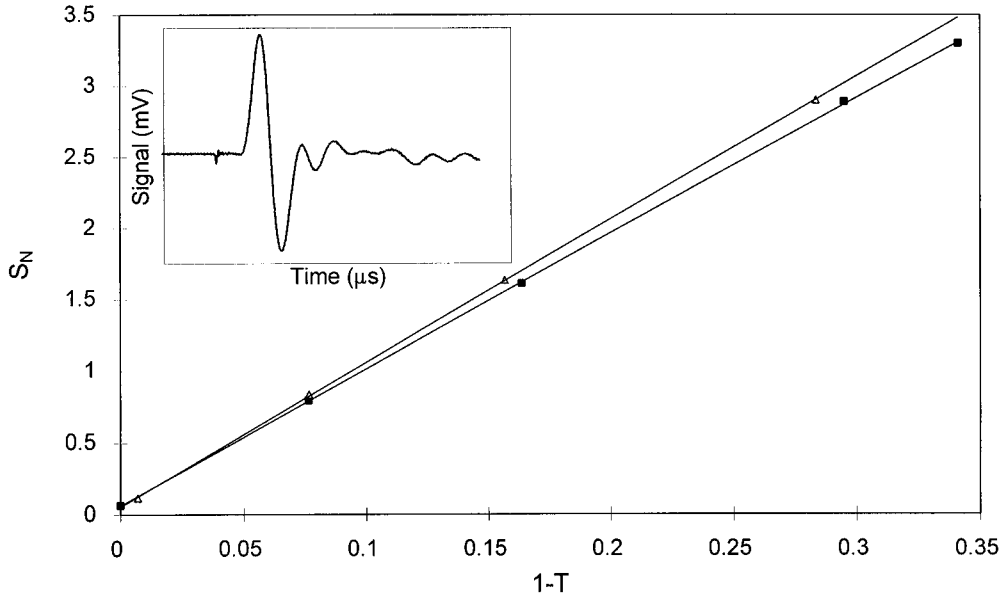


FIGURE 2. Typical plot for a photoacoustic experiment with a mixture of di-*tert*-butyl peroxide and phenol (0.1 M) in benzene. Linear relations between S_N (S_{obs} normalized for laser energy fluctuations) and absorbed light ($1 - T = 1 - 10^{-A}$) are shown for the calibration compound 2-hydroxybenzophenone (■) and for phenol (△). The ratio $a_{obs}/a_{cal} = f_{obs} = 1.056$. With eqs 6 and 11, a photon energy, $E_{h\nu}$, of 84.8 kcal mol^{-1}, $\Phi = 0.83$, and ΔH(PhOH···S) = 1 kcal mol^{-1}, BDE(O−H) in phenol is 87 ± 1 kcal mol^{-1}. Insert: The actual photoacoustic signal as monitored by the piezoelectric microphone. The peak-to-peak amplitude of the first oscillation equals S_{obs}. Other oscillations originate from shock waves reflected from the wall of the photoacoustic cell.

Retrieving the Reaction Enthalpy

In the absence of radiative decay (i.e., luminescence), the heat released is related to the absorbed energy, $E_{h\nu}(1 - 10^{-A})$, the enthalpy of the reaction in solution, $\Delta_r H^{sol}$, and the photochemical quantum yield, Φ (eq 5). However,

$$\Delta_r H^{sol} = \frac{(1 - f_{th})E_{h\nu}}{\Phi} \qquad (5)$$

the experiment provides a value of f_{obs}, not f_{th}, and produces only a measure of the *apparent* reaction enthalpy, $(\Delta_r H)^{sol}_{app}$ (eq 6), which still contains contributions

$$(\Delta_r H)^{sol}_{app} = \frac{(1 - f_{obs})E_{h\nu}}{\Phi} = \Delta_r H^{sol} - \frac{\Delta_r V}{\chi_s} \qquad (6)$$

from the reaction volume change, reinforcing the fact that the observed signal contains more information than the reaction enthalpy alone. The apparent reaction enthalpy is described by eq 6, which depends on three parameters: Φ, $\Delta_r V$, and $\Delta_r H$. Knowledge of any two of these allows the third to be determined. Since one normally is interested in the enthalpy, independent measurements or estimates of the quantum yield and reaction volume are imperative. Indeed, we have also used this expression to determine $\Delta_r V$ for the photodissociation of di-*tert*-butyl peroxide, for which the enthalpy is well-known (vide infra).

The value of f_{obs} is determined by establishing the linear relationship (eq 4) between the signal (S_{obs}) and the amount of light absorbed by the sample ($1 - 10^{-A}$) to yield a slope $a_{obs} = cf_{obs}E_{h\nu}\chi_s$. In practice, this slope is obtained by varying the concentration of the absorbing species or the intensity of the incident light. The photoacoustic response is normalized for variations in the laser intensity by dividing the observed signal by the measured laser pulse energy. The instrument is calibrated by comparing the photoacoustic signal from the sample with that from a compound that returns all absorbed light as heat. A number of suitable calibration compounds for organic solvents and aqueous systems have been tabulated elsewhere.[19] We have used ferrocene and 2-hydroxybenzophenone for photolysis at 337 nm (nitrogen laser) in organic solvents. Since there is no accompanying volume change associated with the calibration response, $f_{obs} = f_{th} = 1$. The value of f_{obs} for the sample in question is simply the ratio of the slopes for the sample, a_{obs}, and the calibration compound, a_{cal} ($f_{obs} = a_{obs}/a_{cal}$). Thus, for an exothermic reaction, more energy is returned than supplied to the system and f_{th} (but not necessarily f_{obs}, eq 6) is larger than unity. Great care must be taken to ensure that the values of c and χ_s are the same during calibration and sample measurement. An example of the resulting plots is shown in Figure 2. Errors can be minimized by signal averaging. It is essential that linear plots of S_{obs} vs $(1 - 10^{-A})$ are obtained. In our experience, linear regression coefficients, r^2, of 0.9996 are routinely achieved, leading to an error in $(\Delta_r H)^{sol}$ of ±1.5 kcal mol^{-1}.

Bond Dissociation Enthalpies

By use of reactions 7 and 8, the R−H bond dissociation enthalpy can be determined since PAC can measure the

enthalpy for the overall process (reaction 9). It is clear

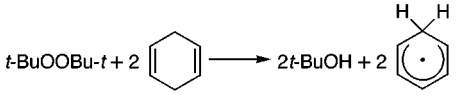
$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^{\bullet} \qquad (7)$$

$$t\text{-BuO}^{\bullet} + \text{RH} \rightarrow t\text{-BuOH} + \text{R}^{\bullet} \qquad (8)$$

$$t\text{-BuOOBu-}t + 2\text{RH} \xrightarrow{h\nu} 2t\text{-BuOH} + 2\text{R}^{\bullet} \qquad (9)$$

that measuring the enthalpy for the overall reaction (9) is quite a long way from actually determining the bond dissociation enthalpy. To obtain the BDE in solution, $\Delta_r V/\chi_s$ (eq 6) needs to be independently determined. According to eq 6, a plot of $(\Delta_r H)_{\text{app}}^{\text{sol}}$ vs $1/\chi_s$ should give a straight line with slope $\Delta_r V$ and intercept $\Delta_r H^{\text{sol}}$. Herman and Goodman[21] and Hung and Grabowski[23] varied χ_s by applying a homologous range of solvents or solvent mixtures. We measured the quantum yield for the photodissociation of di-*tert*-butyl peroxide (reaction 7) in various solvents. Since the thermochemistry for the dissociation ($\Delta_7 H = 38$ kcal mol^{-1}) is known, it was possible to calculate the values for $\Delta_7 V/\chi_s$ from eq 6, using the f_{obs}. We showed that the $\Delta_7 V = 12.4$ mL mol^{-1}, independent of the solvent.[24]

A second complication to overcome lies in the fact that the peroxide and alcohol in eq 9 are in solution while their available heats of formation pertain to the gas phase. The change in solvation enthalpy associated with the conversion of 1 mol of di-*tert*-butyl peroxide into 2 mol of *tert*-butyl alcohol in a given solvent can, in principle, be measured by solution calorimetry. However, it is not necessary to actually measure these values. Our research groups have followed a rather pragmatic approach to resolve this difficulty.[24] To retrieve a bond dissociation enthalpy, a solvent-dependent correction term, $(\Delta\Delta_s H)_{\text{app}}$, to include the reaction volume change ($\Delta_r V$) and the change in solvation enthalpies ($\Delta_s H$), was developed. By studying the reaction of di-*tert*-butyl peroxide with 1,4-cyclohexadiene (eq 10), we could determine $(\Delta\Delta_s H)_{\text{app}}$ in



(10)

various solvents. This approach is based on the key assumption that the C−H bond enthalpies in the gas phase (76 kcal mol^{-1})[25] and in solution are the same. Accordingly, the difference between $(\Delta_{10}H)_{\text{app}}^{\text{sol}}$ and the known gas phase value for $\Delta_{10}H^{\text{gas}}$ provides the solvent correction factor for a particular solvent. We have found these values to be remarkably constant, ranging from −9 kcal mol^{-1} in nonpolar solvents to −13 kcal mol^{-1} in polar solvents (see Table 1). Thus, a simple expression for the bond energy, BDE(R−H)$^{\text{sol}}$, can be derived by collecting the known heats of formation and the empirical correction factor for the solvent (eq 11). In this equation, the

$$\text{BDE(R}-\text{H)}^{\text{sol}} = \frac{(\Delta_9 H)_{\text{app}}^{\text{sol}}}{2} - \frac{(\Delta\Delta_s H)_{\text{app}}}{2} + 86.0 \qquad (11)$$

Table 1. Solvent Correction Factors, $(\Delta\Delta_s H)_{\text{app}}$, for PAC[a]

solvent	$(\Delta_{10}H)_{\text{app}}^{\text{sol}}$	$(\Delta\Delta_s H)_{\text{app}}$[b]	$\Delta_7 V/\chi_s$[c]
isooctane	−30	−10	5.8
carbon tetrachloride	−29	−9	3.2
benzene	−29	−9[d]	3.7
acetonitrile	−33	−13[d]	3.8
ethyl acetate	−33	−13	3.8

[a] Reaction 10; average of at least four independent determinations; enthalpies in kcal mol^{-1}. The experimental error is 2 kcal mol^{-1}.[24] [b] In the gas phase, the BDE(C−H) of 1,4-cyclohexadiene is 76 kcal mol^{-1},[25] leading to $\Delta_{10}H^{\text{gas}}$of −20.3 kcal mol^{-1}. [c] Assuming an average value of $\Delta_7 V = 12.4$ mL mol^{-1}. [d] Similar values has been found for tetralin (−9) and tetrahydrofuran (−13).[30]

constant of 86.0 kcal mol^{-1} encompasses the relevant gas phase heats of formation for *tert*-butyl alcohol,[26a] the hydrogen atom,[26a] and di-*tert*-butyl peroxide[26b] of −74.7, 52.1, and − 81.6 kcal mol^{-1}, respectively, at 298 K.

Solvent Effects on Bond Energies

In the determination of the solvent correction factors, the explicit assumption has been made that the heats of solvation for 1,4-cyclohexadiene and cyclohexadienyl are not significantly influenced by the nature of the solvent, in agreement with guidelines previously suggested by Griller and co-workers.[27] These simple guidelines state that (1) heats of radical reactions in nonpolar solvents will be the same as those in the gas phase and (2) heats of free radical reactions in polar solvents will differ from those in the gas phase to an extent that reflects the solvation energies associated with the net formation or destruction of polar species. Indeed, remarkably good agreement can be found for C−H bond enthalpies determined in the gas phase and in solution using PAC or electrochemical methods. Obviously, this assumption does not hold for the transformation of the peroxide into *tert*-butyl alcohol. The latter has an appreciable dipole moment, and the heat of solvation will depend on the solvent used. From Table 1 it can be inferred that since the chemical volume change remains fairly constant, the change in $\Delta\Delta_s H$ is directly related to the increase in the solvation enthalpy of the alcohol.

The enthalpy measurements become even more complicated when hydrogen bonding takes place between the compound of interest and the solvent. As an example, we studied the BDE(O−H) in phenol. Hydrogen abstraction by the *tert*-butoxyl radical only occurs with the non-hydrogen-bonded fraction of phenol, and therefore the measured enthalpy change now includes the solvent/solute equilibrium. Consequently, the apparent O−H bond strength of phenol is higher in acetonitrile than in benzene, due to an additional hydrogen-bonding enthalpy (Table 2).[24] However, after introducing the known enthalpy change associated with the formation of a hydrogen bond, we were able to arrive at one gas phase bond enthalpy in all solvents in good agreement with the accepted literature value of 87 kcal mol^{-1}.[24]

Table 2. Solution Bond Dissociation Enthalpies, BDE((O−H)^{sol}, for Phenol[a]

solvent	$(\Delta_9H)^{sol}_{app}$	BDE(O−H)^{sol}	ΔH(PhOH···S)	BDE(O−H)$^{sol}_{corr}$ [e]
isooctane	−9.8	86.2	0[c]	86.2
carbon tetrachloride	−5.1	88.0	0[d]	88.0
benzene	−6.5	87.3	1.0	86.3
acetonitrile	0.8	93.0	4.7	88.3
ethyl acetate	0.7	93.0	4.7	88.3
dimethyl sulfoxide		94[b]	6.6	
triethylamine		96[b]	8.9	
solution				av 87.4
gas phase				87[f]

[a] Data from ref 24; all energies are in kcal mol^{-1}. For simplicity, the bond energies are defined with the standard state of the hydrogen atom being 298 K in the gas phase rather than in solution as was defined in ref 24. [b] Estimated from the known enthalpy of hydrogen bond formation (Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875−3891) by following the procedure in ref 24. [c] Assumed. [d] By definition. [e] Solution bond energy corrected for hydrogen bonding to the solvent calculated by subtracting from BDE(O−H)^{sol} the enthalpy of hydrogen bond formation between the phenol and the solvent. [f] Arends, I. W. C. E.; Louw, R.; Mulder, P. *J. Phys. Chem.* **1993**, *97*, 7914−7925.

Time Resolution and Parallel/Consecutive Processes

The time resolution of a PAC experiment is determined by the acoustic transit time $\tau_a = R/v_a$ (R = laser beam radius, v_a = speed of sound in the medium). Braslavski and Heibel[19] suggested a time resolution (τ_{eff}) of $1.47\tau_a$ or $2\tau_a$: all heat released within this time is integrated and included in the prompt heat release f_{obs}. For a laser beam width of 1 mm and v_a varying from 900 to 1400 m s^{-1} in organic solvents, τ_{eff} is around 10^{-6} s. Hence, the lifetime for the *tert*-butoxyl radical in the reaction sequence employed, $1/(k_8[RH])$, should be at most $0.2\tau_{eff}$ to ensure that more than 99% of the reaction heat is detected. By varying τ_{eff} (i.e., changing the laser beam radius), one can cause different parts of the exponential decay to fall within the prompt heat domain which can be used to determine the reaction time scales.[28]

The success of a photoacoustic experiment depends on knowing the reaction rate in relation to the heat integration time. If a reaction (i.e., the heat deposition) is too slow, it will not be completed before the heat integration time lapses. In this case, the observed signal is actually a convolution of the chemical decay rate with the instrument response function. On the other hand, if the primary reactions are fast enough, subsequent reactions may contribute to the heat integration, changing the amplitude of the photoacoustic signal. In fact, it is this effect that allows one to use eqs 7 and 8 to determine the bond energy.

Using standard kinetics theory, the heat that is expected from a certain reaction or reaction sequence can be predicted. The photodissociation of di-*tert*-butyl peroxide is instantaneous, resulting in initial concentrations of *tert*-butoxyl radicals in the irradiated volume of approximately 10^{-6} M. The rate constants of the subsequent hydrogen abstractions are usually known from the literature. For example, the abstraction of a hydrogen atom from phenol, with a rate constant of 3.3×10^8 M^{-1} s^{-1} in benzene,[29] is fast enough to deliver all reaction heat ($\Delta_8H = -18$ kcal mol^{-1}) within the photoacoustic time window, even at low phenol concentrations. However, the abstraction of the benzylic hydrogen from toluene ($\Delta_8H = -16$ kcal mol^{-1}), with a rate constant of 2.3×10^5 M^{-1} s^{-1},[29] is too slow, even in neat toluene (Figure 3). With a photoacoustic time window of 1 μs, only fast processes are observed. Therefore, even if the concentration of R$^\bullet$ were to rise to as high as 10^{-6} M, radical−radical coupling will not contribute to the observed signal, despite the diffusion-controlled rate constant.

In the determination of the α-C−H bond strength in tetralin (TET),[30] with a low rate constant for hydrogen abstraction, the time limitation was circumvented by adding a second reactant, tetrahydrofuran (THF), with a known bond strength and a known higher reaction rate constant. The result of this competitive hydrogen atom abstraction process is that the lifetime of the *tert*-butoxyl radical remains well within the photoacoustic time domain. Under these conditions, the fraction of the observed reaction enthalpy from each of the competing processes is determined by the rates of the two individual reactions (eqs 12 and 13). A plot of Δ_9H^{sol} against ξ yields a straight

$$\Delta_9H^{obs} = \xi\Delta_9H^{TET} + (1 - \xi)\Delta_9H^{THF} \qquad (12)$$

$$\xi = \frac{k_8^{TET}[TET]}{k_8^{TET}[TET] + k_8^{THF}[THF]} \qquad (13)$$

line with a slope that depends on the difference in reaction enthalpy for the two processes. If these enthalpies are exactly known, it is possible to determine the kinetics for one of the competing reactions (i.e., ξ is unknown). On that basis, we have demonstrated[30] that, with a high (>2 M) reactant concentration, the rate constant for hydrogen abstraction is around 40% lower than the literature value. The rate constants for reaction 8 are usually measured by means of laser flash photolysis (LFP) at low substrate concentrations. The apparent deviation can be ascribed to the operation of bulk solvent properties (e.g., activities instead of concentrations). Hence, PAC can also been applied to retrieve rate constants under conditions which are not accessible by conventional methods.

Revised Bond Dissociation Enthalpies

A variety of organic and organometallic compounds have been studied with PAC in our laboratories in the past decade, demonstrating the applicability of the technique

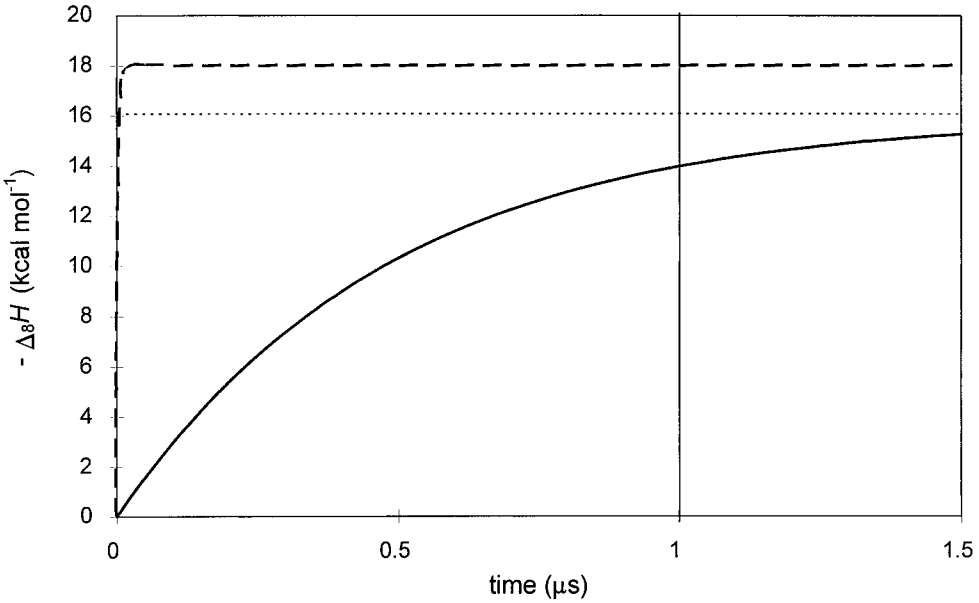


FIGURE 3. Release of reaction enthalpy for hydrogen abstraction from 0.1 M phenol (−−) and neat, 9 M, toluene (—) as a function of the integration time for the detector. The vertical line at 1 μs denotes the limit of the prompt heat domain (τ_{eff}) for photoacoustic calorimetry. The dotted horizontal line (•••) represents the final reaction enthalpy with toluene.

to retrieve bond dissociation enthalpies, reaction volumes, and kinetic information. However, some of the earlier results should be treated with caution since not all of the above considerations were incorporated in the data analyses. In the earlier publications, reaction volume effects and heats of solvation were generally not considered and in some cases they were assumed to be negligible. Table 3 lists the bond dissociation enthalpies that were determined using PAC, by following the basic method outlined in the first part of this Account. PAC literature data[31] for a number of ligand−metal BDEs are not included. Where possible, revised bond strengths are given, based upon the reported values for f_{obs}, but applying the correct quantum yield (see Table 3, footnote *a*), the constant 86.0, and the solvent correction factor $(\Delta\Delta_s H)_{app}$ according to eq 11.

From the original work of Griller,[3] revised bond dissociation enthalpies of 79 and 77 kcal mol^{-1} are obtained for Bu_3Sn-H and 1,4-cyclohexadiene, respectively. Due to incompatibly slow kinetics for the hydrogen atom abstraction from diethyl ether, we are not able to reevaluate the enthalpy of this process.

In isooctane, a Si−H bond strength of 90 kcal mol^{-1} has been reported for triethylsilane (entry 4),[32] which at that time was in line with the known heats of formation of silanes and silyl radicals. Revision leads to 96 kcal mol^{-1}, which is in close agreement with the now accepted BDE(Si−H) bond strength of 95 kcal mol^{-1}.[33]

The reported O−H bond strengths[7,34] (entries 7 and 8) in phenol are clearly too low. Reconsideration yields a BDE of 87 kcal mol^{-1}, which is perfectly in line with the results published a few years later (entry 9).[24] We also studied the effect of ring substitution on the O−H bond strength, resulting in a correlation between ΔBDE(O−H) and the Hammett σ^+ constant.[34] This correlation was later extended to a wider range of phenols, including the tocopherols.[35]

In a study of the α-C−H bond strength in a number of alcohols (entries 10−14), using photolysis of hydrogen peroxide in water as the radical source, Kanabus-Kaminska et al.[27] showed that the difference in solvation enthalpies between hydrogen peroxide and water must be incorporated in the analysis. However, the absolute bond dissociation enthalpies are still not compatible with the most recent gas phase values. For comparison, the accepted BDE(C−H) for methanol[4] is 96.1 kcal mol^{-1}, while PAC renders a value which is 4 kcal mol^{-1} lower. It is probable that the reason for the discrepancy is the unknown contribution of the reaction volume change in this solvent mixture.

Due to the sluggishness of the hydrogen abstraction by the hydroxyl radical from CH_3CN (entry 15) and CH_3COO^- (entry 16), a competitive hydrogen abstraction from hydrogen peroxide takes place (eq 14).[27] However, the enthalpy for reaction 14 in solution is not known so the two competing contributions cannot be separated at this time.

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad (14)$$

To determine the heat of formation of the benzoyl radical, triethylsilane has been introduced as a coreactant,[37] in order to ensure a fast halogen atom abstraction from benzoyl chloride (eqs 15 and 16). This procedure has also been applied to sulfonyl chlorides[42] and benzyl bromides.[43]

$$t\text{-BuO}^{\bullet} + Et_3SiH \rightarrow t\text{-BuOH} + Et_3Si^{\bullet} \qquad (15)$$

$$Et_3Si^{\bullet} + PhC(O)Cl \rightarrow Et_3SiCl + PhC(O)^{\bullet} \qquad (16)$$

Table 3. Bond Dissociation Enthalpies, BDE, Determined by PAC in kcal mol^{-1} at 298 K

entry	compound	solvent	BDE[a]	ref	BDE[a] revised
1	$(C_4H_9)_3Sn-H$	isooctane	74	3	78
2	1,4-c-C_6H_7-H	isooctane	73	3	77
3	$C_2H_5OCH(-H)CH_3$	isooctane	93	3	
4	$(C_2H_5)_3Si-H$	isooctane	90	32	96[b]
5	$(CH_3)_3Si(CH_3)_2Si-H$	isooctane	85	32	91
6	$((CH_3)_3Si)_3Si-H$	isooctane	79	32	84[b]
7	C_6H_5O-H	benzene	84	2	c
8	C_6H_5O-H	benzene	84	34	87[d]
9	C_6H_5O-H	various	87	24	87[d]
10	$CH_2(-H)OH$	water	92	27	*e*
11	$CH_3CH(-H)OH$	water	92	27	*e*
12	$(CH_3)_2C(-H)OH$	water	89	27	*e*
13	$(CH(-H)OH)_2$	water	90	27	*e*
14	$(CH_2(-H))_3OH$	water	99	27	*e*
15	$CH_2(-H)CN$	water	96	27	*e*
16	$CH_2(-H)COO^-$	water	92	27	*e*
17	DHA (C_9-H)[f]	benzene	78	36	*g*
18	9,9-$(CH_3)_2$DHA ($C_{10}-H$) [f]	benzene	77	36	*g*
19	$PhC(O)-Cl$	benzene	81	37	87
20	$(C_2H_3)_2C(-H)H$	benzene	77	38	*h*
21	$(C_2H_3)_2C(-H)CH_3$	benzene	77	38	*h*
22	$(C_2H_3)_2C(-H)OH$	benzene	69	38	*h*
23	$(CH_3)_3Ge-H$	benzene	82	39	87[b]
24	$(C_2H_5)_3Ge-H$	benzene	82	39	86[b]
25	$(C_4H_9)_3Ge-H$	benzene	83	39	88[b]
26	$(C_6H_5)H_2Ge-H$	benzene	79	39	86
27	$(C_6H_5)_2HGe-H$	benzene	80	39	85
28	$(C_6H_5)_3Ge-H$	benzene	80	39	85
29	$(CH_3S)_3Si-H$	benzene	83	40	87
30	(i-$C_3H_7S)_3Si-H$	benzene	86	40	90
31	$(CH_3)_2NCH_2-H$	benzene	87	41	91[i]
32	2-oxomorpholine[j] (C_3-H)	benzene	75	41	78[i]
33	morpholine (C_3-H)	benzene	91	41	94[i]
34	piperazine (C_2-H)	benzene	90	41	93[i]
35	$(CH_3)SO_2-Cl$	benzene	70	42	70[k]
36	$(C_6H_5)SO_2-Cl$	benzene	71	42	71[k]
37	tetrahydrofuran (C_2-H)	THF	92	30	92
38	tetralin (C_1-H)	tetralin	83	30	83
39	$C_6H_5CH_2-Br$	various	61	43	61
40	C_6H_5NH-H	benzene	90	44	90[l]
41	$(C_6H_5)_2N-H$	benzene	87	44	87[m]

[a] Reported BDEs in the original papers; where possible, these values have been reevaluated according to eq 11 and employing the quantum yield for the photodissociation of the di-*tert*-butyl peroxide: $\Phi_{benzene} = 0.83$, or $1/(1-\Phi) = 2.6\exp(0.48/\eta)$ with η the viscosity (in cP) of the medium.[24] Error margins are 1.5 kcal mol^{-1}. [b] The small contribution, within error margins, for side chain hydrogen abstraction is not included. [c] Time-resolved PAC, deconvolution method. [d] Substituted phenols have been studied on several occasions, yielding the following ΔBDEs (kcal mol^{-1}): 4-CN, 5.6; 4-CF_3, 3.2; 4-Cl, 0.4; 4-*t*-Bu, −1.9; 4-MeO, −5.8; 2,4,6-Me_3, −5.5; 2,6-(*t*-Bu)$_2$-4-Me, −7.7; 2,4-(*t*-Bu)$_2$, −5.2; 2,6-Me_2-4-MeO, −10.1; γ-tocopherol, −7.1; α-tocopherol, −10. See refs 34 and 35. [e] See text. [f] DHA = 9,10-dihydroanthracene; 9,9-$(CH_3)_2$DHA = 9,9-dimethyl-9,10-dihydroanthracene. [g] Substrate concentrations were chosen too low compared to the PAC time window. [h] Values after evaluation are 82, 82, and 74.0 kcal mol^{-1}, respectively. However, addition of *t*-BuO$^\bullet$ to the double bond takes place as well, and the two processes cannot be disentangled (see text). [i] A volume correction of +2.1 kcal mol^{-1} was already incorporated in the original paper. [j] A number of substituted oxymorpholines and related compounds have been studied as well.[41] [k] Measured relative to CCl_4; solvation correction is not necessary. [l] Substituent effects in ΔBDE (kcal mol^{-1}): 4-Me, −2.2; 4-F, −0.9. [m] ΔBDE for 4,4′-Me_2: −1.0 kcal mol^{-1}.

The carbon−hydrogen bond dissociation enthalpy in 1,4-pentadiene[38] was found to be compatible with that obtained from gas phase thermolysis [45a] (76 kcal mol^{-1}). Reevaluation of the original PAC data shows that the BDEs in the (substituted) pentadienes (entries 20−22) are too high (e.g., BDE(C−H) in pentadiene: 82 kcal mol^{-1}). Addition of a *tert*-butoxyl radical to the double bonds[45b] is a competing reaction, which may occur to an extent of 10−20% of the overall reaction. This addition is less endothermal than the abstraction from the methylene hydrogen, and according to eq 11, $\Delta_r H^{sol}$ increases, which leads to an overestimation of the BDE(C−H). Upon substitution of the methylene group by OH (compare entries 20 and 22), the rate for hydrogen abstraction increases and the relative contribution of the addition process decreases. The latter example underscores the requirement to know the kinetics in some detail in order to use the PAC technique.

Concluding Remarks

Over the past decade, photoacoustic calorimetry has matured into a versatile tool for thermodynamic and kinetic measurements in a broad range of disciplines. It provides fundamental information concerning inter- and intramolecular interactions and chemical transformations. Reaction enthalpies *in solution* on a microsecond time scale can now be established accurately by adopting the straightforward experimental approach described in this Account. Most importantly, reaction enthalpies in solution

can be determined directly, thus obviating the need to convert gas phase properties to those in solution. Fortunately, in most cases there is good agreement between gas phase and liquid phase BDEs. However, this is not the case for hydroxylic and other acidic X−H bonds. While this Account has focused on the application of PAC for the determination of bond dissociation enthalpies, other physicochemical properties such as the magnitude of hydrogen bonding between the solute and solvent or the chemical volume change can be retrieved by the same method. In the future, we expect the application of PAC to extend from merely fundamental aspects of chemical reactions into areas of applied chemistry and biochemistry.

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