

α -C–H Bond Strengths in Tetralin and THF: Application of Competition Experiments in Photoacoustic Calorimetry

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Photoacoustic Calorimetry is used to determine the α -C–H bond dissociation Energy (BDE) in 1,2,3,4-tetrahydronaphthalene (tetralin) in the neat liquid as well as in competition with hydrogen abstraction from tetrahydrofuran (THF). Also, the α -C–H BDE in THF was determined in the neat liquid. The experiments with the mixtures of tetralin and THF and with the neat liquids lead to the same results. $\text{BDE}^{\text{gas}}(\text{tetralin})$ is found to be 82.9 ± 1.2 and $\text{BDE}^{\text{gas}}(\text{THF})$ to be 92.1 ± 1.6 kcal mol⁻¹. The revised global rate constant of hydrogen abstraction from THF is found to be 4.6×10^6 M⁻¹ s⁻¹ at 297 K.

Introduction

Tetralin (1,2,3,4-tetrahydronaphthalene), due to its easily abstractable α -hydrogens, is frequently used as a hydrogen donor solvent and a radical carrier in coal-liquefaction studies.^{1–3}

Interestingly though, the benzylic C–H bond strength in tetralin has never been determined directly, and an explanation for its reactivity is usually derived from structurally analogous compounds. Thus, Stein and Brown⁴ assessed a bond strength of 86.7 kcal mol⁻¹ applying an empirical relationship between calculated variations in π -electron differences and bond energy increments in a series of aromatic hydrocarbons.

Recently, it has been demonstrated⁵ that in a series of hydroaromatics (RH) the rate constants for benzylic type hydrogen abstraction by *tert*-butoxyl radicals (eq 2) in the liquid phase can be correlated with the reaction enthalpies, ΔH_2 , and thus with the bond dissociation energies (BDEs) of R–H. The data obey an Evans–Polanyi relationship⁶ to yield $E_a = 0.21\Delta H_2 + 7.9$. The α -C–H bond dissociation energy in tetralin used in this case was considered equal to that in ethylbenzene (85 kcal mol⁻¹).⁵

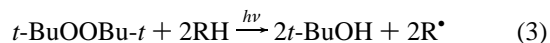
However, using these values in the Evans–Polanyi relationship, the data point for tetralin clearly deviates from this correlation. Because the H abstraction rate constants (k_2) have been determined accurately with laser photolysis,⁵ it may be that the α -C–H BDE in tetralin is lower than that assumed previously.

Various methods are conceivable to determine the bond strength, such as gas phase thermolysis methods (*e.g.*, shock tube or very low pressure pyrolysis). Determination of, for instance, the strength of the benzylic C–CH₃ bond in the α -methyl derivative of tetralin could provide the required information in an indirect way. However, in this case another unimolecular decomposition route (elimination of ethene) obscures the thermal decay by C–CH₃ cleavage.⁹

These findings prompted us to determine the α -C–H bond dissociation energy in tetralin in the liquid phase using photoacoustic calorimetry (PAC). Photoacoustic calorimetry has already been proven to be successful in the direct determination of various BDEs in the liquid phase,¹⁰ and the appropriate correction factors for solvation have been derived to allow extrapolation to the gas phase.^{10c}

With PAC the overall reaction enthalpy can be determined for a sequence of reactions involving the laser-induced photo-

dissociation of di-*tert*-butyl peroxide and hydrogen abstraction (reactions 1 and 2):



The origin of the photoacoustic signal is a local expansion of the solution caused by the heat generated by the process. The signal is directly proportional to the enthalpy, ΔH_3 , for the overall reaction 3.

An important restriction in PAC is the time window in which the heat deposition must be completed. This time window is given by the effective acoustic transit time τ_a' ,¹¹ which is determined by the laser beam width and the velocity of sound, v_a , in the medium. Typically in organic solvents with $v_a = 1300$ m s⁻¹ and a laser beam width of 1 mm, τ_a' is about 750 ns. To ensure that more than 99.4% of the reaction heat is detected, the life time of the *tert*-butoxyl radical ($\tau_{t\text{-BuO}^\bullet} = 1/k_2[\text{RH}]$) should be at maximum $0.2 \tau_a'$. This leads to an operational criterium for PAC that $\tau_{t\text{-BuO}^\bullet}$ must be shorter than 150 ns. Heat deposition which takes longer than τ_a' contributes only through an exponential decay function to the PAC signal.

Therefore, with a rate constant⁵ for reaction 2, where R–H is tetralin, of 8.3×10^6 M⁻¹ s⁻¹, a high concentration of Tetralin is needed. Alternatively, a second reactant with abstractable hydrogens could be added to reduce the lifetime of the *tert*-butoxyl radicals. The photoacoustic signal then represents a combination of two reaction enthalpies. If the thermodynamics and kinetics of the second reaction are known, the required enthalpic information can be retrieved.

In this study the α -C–H bond strength in tetralin is determined with PAC following these two approaches: using neat tetralin (a concentration of 7.4 M) and in competition with α -hydrogen abstraction from tetrahydrofuran (THF). THF mixes with tetralin in all proportions, and the abstraction rate constant for THF is known. In the course of this investigation also the α -C–H bond dissociation energy in THF has been determined.

Experimental Section

Photoacoustic Calorimetry. The photoacoustic apparatus has been described before.^{10c} It consists of a standard fluores-

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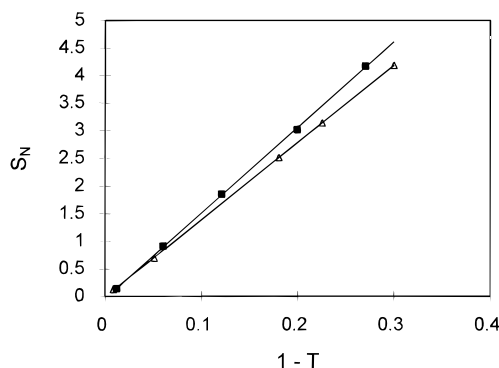


Figure 1. Typical plot from a photoacoustic experiment: an experiment with 0.94 M THF and 6.80 M TET; $f_{\text{obs}} = 1.11$; Δ calibration; \blacksquare sample measurement.

cence cuvette (Hellma 221), modified to allow continuous flow experiments, containing solutions of di-*tert*-butyl peroxide and (mixtures of) 1,2,3,4-tetrahydronaphthalene and THF. After deoxygenation by purging with argon, the solutions were photolyzed using 600 ps pulses from a PRA LN 1000 nitrogen laser (337.1 nm, 84.8 kcal mol⁻¹). The resulting shock wave was detected by a Panametrics Model V101, 1 MHz, piezoelectric transducer in contact with the bottom of the cell (with a thin layer of vacuum grease to provide good acoustic transmission). The signals were amplified (Panametrics Model 5670 ultrasonic preamp) and digitized (Tektronix Model 2430A Digital Oscilloscope). The signal to noise ratio was improved to up to 100:1 by averaging 256 acquisitions. Each data point was determined three times. Fluctuations in the laser energy were monitored using an L-PED pyroelectric device to which 10% of the incident laser beam was directed. The remaining radiation was passed through a 1 mm pinhole in front of the cuvette. The average laser energy in these experiments was <50 mJ/pulse (i.e., flux < 6 mJ/cm⁻²). The photoacoustic cell was located inside an HP 8452A diode array spectrophotometer so that the absorbance of the solution could be measured simultaneously with the PAC signal. The instrument was calibrated using *o*-hydroxybenzophenone in the same mixtures but without the peroxide.

Viscosity Measurements. The viscosities of tetralin and the mixtures with THF were determined at 24 °C using a Haake CV 100 Low Shear Rotation Viscosimeter, equipped with an ME 30 sensor.

Chemicals. All chemicals were obtained from commercial sources.

Tetralin was distilled under reduced pressure and passed over silica (60–200 mesh) prior to use. THF (spectroscopic grade) was distilled prior to use. Di-*tert*-butyl peroxide was vacuum distilled and passed over alumina immediately before use. *o*-Hydroxybenzophenone was recrystallized from ethanol.

Results

PAC with Tetralin and THF. In short, the photoacoustic experiment consists of measuring the signal amplitude for increasing concentrations of *o*-hydroxybenzophenone (calibration) and peroxide. The ratio of the slopes of the two lines thus found is f_{obs} , the apparent amount of light energy returned to the solution as heat.

The resulting lines are straight, indicating that the increasing amount of peroxide (up to 10% v/v) does not significantly affect the (thermo)elastic properties of the solution (see Figure 1).

The reaction enthalpy, ΔH_3^{obs} , can be obtained using eq 4

$$\Delta H_3^{\text{obs}} = \frac{E_{\text{hv}}(1 - f_{\text{obs}})}{\phi} \quad (4)$$

wherein ϕ is the quantum yield of peroxide dissociation and E_{hv} the energy of the laser light.

TABLE 1: Viscosities of Tetralin, THF and Mixtures; Quantum Yields for di-*tert*-Butyl Peroxide Dissociation at 24 °C

mixture		η (cP)	ϕ^a
TET	neat	2.068 ^b	0.69
TET	neat, 26 °C	2.01	0.69
TET	neat, 28 °C	1.96	0.69
THF	neat	0.55 ^b	0.85
TET/THF	8:1		0.70 ^c
TET/THF	4:1		0.70 ^c
TET/THF	3:1	1.602	0.71
TET/THF	1:1	1.265	0.74
TET/THF	1:3	0.796	0.78
TET	+5% peroxide ^d	2.015	0.69
TET	+10% peroxide ^d	1.96	0.69

^a According to $1/(1 - \phi) = 2.6 e^{0.48(1/\eta)}$ (see ref 16). ^b Values from the literature: $\eta(\text{TET}) = 2.003$ and $\eta(\text{THF}) = 0.46$ cP, at 25 °C; Riddick, J. A., Bunger, W. B. *Organic Solvents, Physical Properties and Methods of Purification*, 3rd ed.; Wiley: New York, 1970.

^c Interpolated. ^d % v/v.

The experimental parameter f_{obs} contains the amount of light energy *actually* returned as heat, and a contribution from the chemical volume change caused by the peroxide dissociation.^{10c} Finally, applying eq 5 the gas phase bond dissociation energy can be calculated.

$$\text{BDE}(\text{R-H}) = \frac{\Delta H_3^{\text{obs}}}{2} - \frac{(\Delta \Delta H_s)_{\text{app}}}{2} + 86.0 \quad (5)$$

A solvent dependent factor, $(\Delta \Delta H_s)_{\text{app}}$, is used to correct the reaction enthalpy calculated in eq 4 for the chemical volume change and also includes the difference in solvation enthalpy between the peroxide and the *tert*-butyl alcohol. $(\Delta \Delta H_s)_{\text{app}}$ has been determined previously for a number of solvents.^{10c,12}

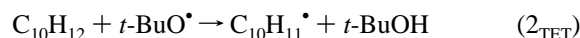
The number 86.0 is a summation of the heats of formation of di-*tert*-butyl peroxide (-81.6 ± 0.5 kcal mol⁻¹),¹³ *tert*-butyl alcohol (-74.7 ± 0.2 kcal mol⁻¹),¹⁴ and the hydrogen atom (52.1 kcal mol⁻¹).¹⁵

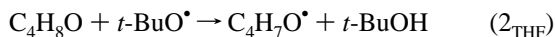
First, the reaction enthalpies $\Delta H_{3\text{TET}}$ and $\Delta H_{3\text{THF}}$ were determined individually. To assure a reaction rate for reaction 3 high enough for the photoacoustic time scale, these experiments were performed in the neat liquids.

The quantum yields were calculated from the relationship between the viscosity of the solution and the cage collapse $(1 - \phi)$ that was established previously¹⁶ from measurements of ϕ in a series of solvents. For that purpose the viscosities of tetralin, THF, and tetralin–THF mixtures have been measured separately and are presented in Table 1 along with the viscosities of mixtures of 5% and 10% di-*tert*-butyl peroxide in tetralin. From these latter data it can be concluded that dissolving up to 1.4 M of peroxide in tetralin (=10% v/v), which is the ultimate concentration of peroxide during a typical PAC experiment, the viscosity does not change significantly. Hence the quantum yield of peroxide dissociation does not change within an experiment. The viscosity change was found to be proportional to the change in the ratio of tetralin/THF in the mixtures.

The heats of reaction applying the neat compounds were found to be $\Delta H_{3\text{TET}} = -1.40 \pm 0.9$ kcal mol⁻¹ and $\Delta H_{3\text{THF}} = 0.0 \pm 1.5$ kcal mol⁻¹ (first and last entry in Table 2).

PAC Competition Experiments with Tetralin and THF. The observed reaction enthalpy ΔH_3^{obs} in a photoacoustic competition experiment with two reactants TET and THF can be expressed as a combination of the reaction enthalpies for the individual reactions and the partial rates at which each reactant participates (eq 6).





$$\Delta H_3^{\text{obs}} = \xi \Delta H_{3\text{THF}} + (1 - \xi) \Delta H_{3\text{TET}} \quad (6)$$

ξ is defined as the fraction of the overall reaction rate accounted for by one of the compounds according to the respective concentrations and rate constants k_{TET} and k_{THF} .

$$\xi = \frac{k_{2\text{THF}}[\text{THF}]}{k_{2\text{THF}}[\text{THF}] + k_{2\text{TET}}[\text{TET}]} \quad (7)$$

If ΔH_3^{obs} is plotted against ξ , a straight line is expected. Rewriting eq 6 into eq 8 shows that a linear relationship should be obtained:

$$\Delta H_3^{\text{obs}} = \Delta H_{3\text{TET}} + \xi(\Delta H_{3\text{THF}} - \Delta H_{3\text{TET}}) \quad (8)$$

The intercept of this plot gives $\Delta H_{3\text{TET}}$, and from the slope the difference in reaction enthalpy is obtained; hence, both $\Delta H_{3\text{TET}}$ and $\Delta H_{3\text{THF}}$ can be retrieved.

On the other hand, if the thermodynamics of both reactions are known, via ξ kinetic information can be deduced from the competition experiments.

An important advantage of this experimental approach is the reduction of the lifetime of the *tert*-butoxyl radicals in the hydrogen abstraction experiments. This method can therefore be applied whenever the reaction rate (and hence the heat deposition) of a compound under study is too slow for a normal, single-compound PAC experiment, since part of the reaction enthalpy will then be released outside the photoacoustic time window.

To retrieve kinetic information, it is of course important that the thermochemistry of both reactions is known accurately, as well as the rate constant of the fast reaction. If $1/\xi$ is plotted against the ratio of concentrations of the reactants, again a straight line is to be found with a slope k_{rel} . For the general case

$$\frac{1}{\xi} = 1 + \frac{k_{\text{A}}[\text{A}]}{k_{\text{B}}[\text{B}]} \quad (9)$$

ξ is determined from eq 8. The intrinsic large error in ΔH_3^{obs} (ca. 1 kcal mol^{−1}) dictates that, in order to minimize the error in ξ , the heats of abstraction from the reactants, ΔH_3 , should lie at least 10 kcal mol^{−1} apart.

The range in rate constants that can be determined with this method is not as large as, for instance, with the method of deconvolution of the photoacoustic signal.¹⁷ To determine the slope in eq 9, ΔH_3^{obs} should at least be measured from $\xi = 1$ down to $\xi = 0.8$. Since $1/(k_{\text{A}}[\text{A}] + k_{\text{B}}[\text{B}])$ needs to be shorter than 100 ns, this limits the pseudo-first-order rate constant for the slowest reaction to around $5 \times 10^5 \text{ s}^{-1}$.

The same conditions also apply when only thermodynamic information is required.

ΔH_3^{obs} was determined in mixtures of tetralin and THF in ratios of approximately $8/1$, $4/1$, $3/1$, $1/1$, and $1/3$ (see Table 2). In order to calculate ξ , the rate constants for hydrogen abstraction from tetralin and THF by the *tert*-butoxyl radical are necessary. The abstraction rate for tetralin has been determined in ref 5 to be $8.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. For the abstraction rate for THF, several values are available from the literature. For this study the value, as measured with laser flash photolysis, is selected which is the same as for tetralin;¹⁸ $8.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Both values refer to global rate constants, *i.e.*, the sum of α and β -hydrogen abstraction. ΔH_3^{obs} for each mixture and the

TABLE 2: ΔH_3^{obs} in Experiments with Tetralin, THF, and Mixtures

ξ^a	[THF] ^b (M)	[TET] ^b (M)	no. of expt. ^c	$\Delta H_3^{\text{obs } d}$ (kcal mol ^{−1})	ξ^e (corrected)
0.0	0	7.36	2	-14.0 ± 0.9	0.0
0.12	0.94	6.80	1	-13.3 ± 1.0	0.07
0.20	1.60	6.40	1	-9.0 ± 1.8	0.12
0.25	2.05	6.14	3	-12.0 ± 1.5	0.16
0.50	4.61	4.61	3	-9.0 ± 1.5	0.36
0.75	7.91	2.64	3	-5.0 ± 1.0	0.63
1.00	12.32	0.0	3	0.0 ± 1.5	1.0

^a According to eq 7, $k_{2\text{TET}}/k_{2\text{THF}} = 1$. ^b As prepared by weight, concentrations calculated using densities and molar volumes. ^c Number of experiments. ^d Average of independent determinations; The indicated error limits include statistical and experimental uncertainties. ^e With adjusted kinetics: $k_{2\text{TET}}/k_{2\text{THF}} = 1.8$; see text.

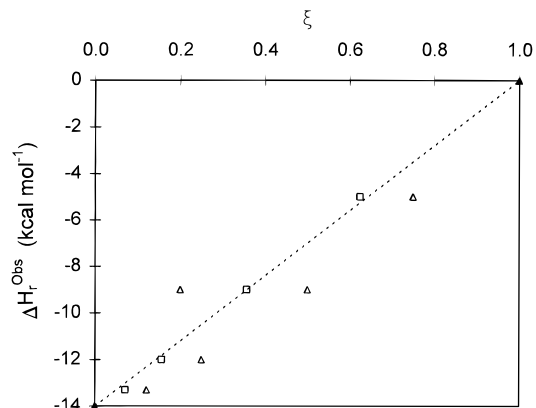


Figure 2. Relation between ΔH_3^{obs} and ξ with tetralin, THF, and mixtures of tetralin and THF. Δ mixtures, $k_{2\text{TET}}/k_{2\text{THF}} = 1$; \blacktriangle neat compounds, \square mixtures, $k_{2\text{TET}}/k_{2\text{THF}} = 1.8$.

results of the photoacoustic experiments on the neat liquids are presented graphically in Figure 2 against the values calculated for ξ .

Discussion

The data in Table 2 are obtained from two separate series of experiments: the results with the neat compounds are independent from those with the mixtures. Therefore it is possible to compare the results from these two series and also verify the reliability of the competition experiments.

The heats of reaction observed in the mixtures of tetralin and THF (Table 2 and Figure 2) show a deviation from the expected linearity (dotted line in Figure 2). The data points all lie below this line and form an almost smooth curve (the data point at $\xi = 0.2$ is ignored). The cause of this deviation could be a gradual change in the solvent composition, changing $(\Delta\Delta H_s)_{\text{app}}$,¹² as the mixture becomes more polar upon addition of THF. Another probable cause is preferential solvation of the peroxide leading to a change in photodissociation characteristics. Manipulation of the data by gradually changing the term $(\Delta\Delta H_s)_{\text{app}}$ did not improve the correlation. A change in the ratio of the rate constants $k_{2\text{TET}}/k_{2\text{THF}}$ from unity to 1.8 (*i.e.*, a change in ξ) however, placed the data points from the mixtures on a straight line.¹⁹ Although the error in the reported rate constants is in the order of $\pm 10\%$,^{5,18} the change in ratio lies well above this experimental uncertainty. The slope of the line is virtually the same as the slope of the line calculated using the reaction enthalpies obtained from the experiments with the neat compounds.

With the adjusted kinetics eq 8 for the experiments with the mixtures becomes

$$\Delta H_3^{\text{obs}} = (14.8 \pm 0.03)\xi - 14.4 \pm 0.01 \quad (R^2 = 1.00) \quad (10)$$

which gives $\Delta H_{3\text{TET}} = -14.4$ and $\Delta H_{3\text{THF}} = 0.4$ kcal mol⁻¹. These values are within the margin of error of the values found in the experiments with the neat compounds.

The change in the ratio of rate constants suggests either a higher k_2 for tetralin or a lower rate constant for THF. The first option seems inappropriate since a higher rate constant for tetralin would case a greater discrepancy between rate constant and bond strength. Moreover, laser flash photolysis measurements using the cumyloxy radical yield a rate constant close to the value for *tert*-butoxy.²⁰ Hence, when the rate constant for tetralin, is accepted, the rate constant for hydrogen abstraction from THF becomes 4.6×10^6 M⁻¹ s⁻¹. Another reported value for hydrogen abstraction is 1.2×10^7 M⁻¹ s⁻¹,²¹ while Malatesta and Ingold²² deduced the abstraction rate from competition experiments with cyclopentane at -60 °C for which extrapolation to room temperature gives $k_{2\text{THF}} = 3.6 \times 10^7$ M⁻¹ s⁻¹. On the other hand, the α -H abstraction from diethyl ether by *tert*-butoxy radicals in solution has a rate constant of 3.6×10^6 M⁻¹ s⁻¹, and the abstraction rate from diisopropyl ether¹⁸ is 1.2×10^6 M⁻¹ s⁻¹ (only two abstractable α -hydrogens).

The increased reactivity of cyclic ethers has been ascribed to the anomeric assistance of the lone pairs of oxygen.²² However, for a species which resembles *t*BuO[•] in reactivity, NO₃, the rate constants for H-abstraction from diethyl ether and from THF in the gas phase were found²³ to be 2.3×10^6 and 2.96×10^6 M⁻¹ s⁻¹, respectively. A comparison between the H-abstraction rates by NO₃ from tetralin and THF in the gas phase shows a similar ratio as found in this study ($k_{\text{TET}}/k_{\text{THF}} = 1.8$).²³

Since the α -C-H bond dissociation energies in the cyclic and acyclic ethers are similar (92 ± 2 kcal mol⁻¹), these data do suggest that a lower rate constant for THF is justified. However, only product studies would yield the most reliable number for relative rates.

Combining the results from both experimental procedures, it can be concluded that the enthalpies for hydrogen abstraction from tetralin and THF are -14.0 ± 0.9 and 0.0 ± 1.5 kcal mol⁻¹, respectively. However, a small adjustment for the contribution of β -hydrogen abstraction is needed.

α and β -Hydrogen Abstraction. Although the abstraction of a β -hydrogen from tetralin or THF is relatively slow, a small portion of the *tert*-butoxy radicals will abstract a β -hydrogen within the photoacoustic time frame. This adds two extra intramolecular competitive reactions to the experiment, and the observed heat of reaction will have to be corrected for these processes.

The bond dissociation energies of the β -C-H in tetralin and THF can be taken to be equal to BDE(C-H) in cyclohexane (98.6 kcal mol⁻¹)²⁴ and cyclopentane (97.6 kcal mol⁻¹)²⁴, respectively. The reaction rate constants for α and β -hydrogen abstraction can therefore be assessed²⁵ to be $k_{2\beta\text{THF}} = 3.4 \times 10^5$ and $k_{2\beta\text{TET}} = 3.3 \times 10^5$ M⁻¹ s⁻¹ resulting in $k_{2\alpha\text{TET}} = 8.0 \times 10^6$ and $k_{2\alpha\text{THF}} = 4.3 \times 10^6$ M⁻¹ s⁻¹. Applying eqs 6 and 7, now for four competitive reactions, the reaction enthalpies for hydrogen abstraction in neat tetralin and neat THF can be calculated.

With $\Delta H_{\beta\text{TET}} = 16.2$ kcal mol⁻¹ (calculated using eq 5 with the appropriate value for $(\Delta\Delta H_s)_{\text{app}}$), this yields for $\Delta H_{\alpha\text{TET}}$

$$\Delta H_{3\alpha\text{TET}} = \frac{\Delta H_{3(\alpha+\beta)} - (1 - \xi)\Delta H_{3\beta\text{TET}}}{\xi} = -15.3 \text{ kcal mol}^{-1} \quad (11)$$

$$(\text{here } \xi = k_{2\alpha\text{TET}}/k_{2(\alpha+\beta)\text{TET}} = 0.96)$$

and for $\Delta H_{\alpha\text{THF}}$ (with $\Delta H_{\beta\text{THF}} = 10.2$ kcal mol⁻¹)

TABLE 3: α -C-H Bond Dissociation Energies for Tetralin and THF^a

	$\Delta H_{3\text{obs}}$	$(\Delta\Delta H_s)_{\text{app}}$	BDE ^{sol b}	BDE ^{gas c}
THF	-0.8 ± 1.5	-13^d	94.1 ± 1.3	92.1 ± 1.6
Tetralin	-15.3 ± 0.9	-9^e	84.9 ± 1.1	82.9 ± 1.2

^a All values in kcal mol⁻¹. ^b According to $\text{BDE}^{\text{sol}} = \Delta H_{3/2} - (\Delta\Delta H_s)_{\text{app}}/2 + \Delta H_s(\text{H}^\bullet) + 86.0$; $\Delta H_s(\text{H}^\bullet)$ is the solvation energy of the hydrogen atom ($=2$ kcal/mol⁻¹).²⁷ ^c According to $\text{BDE}^{\text{gas}} = \text{BDE}^{\text{sol}} - \Delta H_s(\text{H}^\bullet)$. Errors: $(\Delta\Delta H_s)_{\text{app}}$, ± 1 ; 86.0 ± 0.3 kcal mol⁻¹. In view of unknown other uncertainties we have added 0.5 kcal mol⁻¹ to the final statistical error. ^d Using the same value as found in ethyl acetate and acetonitrile.^{10c,12} ^e Using the same value as found in benzene.^{10c,12}

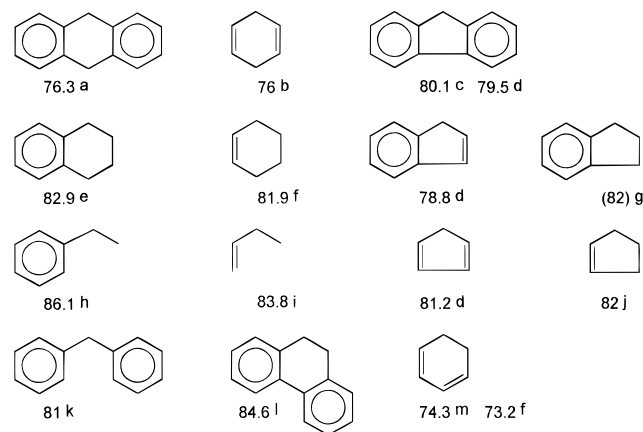


Figure 3. Some α -C-H bond dissociation energies from literature: ^a ref 4; ^b ref 31; ^c ref 32; ^d ref 33; ^e this work; ^f ref 34, estimate; ^g In ref 5 taken to be equal to BDE in cyclopentene; ^h ref 8; BDE(α -C-H) in ethyl benzene reported there is 84.6 kcal mol⁻¹. The relative bond dissociation energies, with a difference between C-H in toluene and ethyl benzene of 2.4 kcal mol⁻¹, presented in ref 8 can be considered accurate. Adjusting the bond strength in toluene to the more recent value³⁰ of 88.5 kcal mol⁻¹ gives $\text{BDE}(\alpha\text{-C-H})$ in ethyl benzene = 86.1 kcal mol⁻¹; ⁱ ref 15; ^j ref 35; ^k ref 4; ^l ref 4, calculated using heats of hydrogenation and hydrogen affinity; a recently³⁶ determined heat of formation of the dihydrophenanthryl radical indicates a bond strength of 81 kcal mol⁻¹; ^m derived from 9,10-dihydrophenanthrene in ref 4.

$$\Delta H_{3\alpha\text{THF}} = \frac{\Delta H_{3(\alpha+\beta)} - (1 - \xi)\Delta H_{3\beta\text{THF}}}{\xi} = -0.8 \text{ kcal mol}^{-1} \quad (12)$$

$$(\text{here } \xi = k_{2\alpha\text{THF}}/k_{2(\alpha+\beta)\text{THF}} = 0.93)$$

From these reaction enthalpies the α -C-H bond dissociation energies can be calculated, using eq 5, for the liquid phase and for the gas phase. These final values are presented in Table 3.

The α -C-H BDE in THF measured three decades ago²⁸ is 92 ± 2 kcal mol⁻¹, and it was recently determined²⁹ to be 93.2 kcal mol⁻¹. The gas phase BDE for THF derived from this study is in perfect accord with these literature data.

The α -C-H BDE found for tetralin is lower than mentioned in the Introduction. The value of 82.9 kcal mol⁻¹, however, still does not fully comply with the higher reactivity.⁵

The C-H Bond Strength in Tetralin. A comparison of the bond strengths in series of some unsaturated hydrocarbons yields the following considerations (see Figure 3). Allylic and benzylic resonance stabilization energies are equal as given by the bond strengths in toluene and propene (88.2 and 88.5 kcal mol⁻¹).³⁰ This also appears to hold for the stabilization energies in cyclic systems: the BDE(C-H) values in 9,10-dihydroanthracene and in 1,4-cyclohexadiene are identical (76 kcal mol⁻¹),^{4,31} and the C-H bond strengths in a series of unsaturated five-membered rings (*i.e.*, fluorene, 79.5 ; indene, 78.8 ; cyclopentadiene, 81.2 kcal mol⁻¹),³³ determined with the electro-

chemical method, are equal within quoted experimental error (± 3 kcal mol⁻¹).

Following this concept, the α -C-H bond strength in tetralin should be compared to the allylic C-H bond in cyclohexene (81.9 kcal mol⁻¹,³⁴ see Figure 3).

Likewise, the series of 9,10-dihydroanthracene (76.3),⁴ tetralin (82.9), and ethylbenzene (86.1)⁸ can be compared to the series 1,4-cyclohexadiene (76),³¹ cyclohexene (81.9),³⁴ and 1-butene (83.8).¹⁵ The differences in BDE between the cyclic and acyclic compounds are small. Given the experimental uncertainties, a further elaboration on these small observed changes as a result of, for example, ring strain appears not to be justified.

Considering these analogies, the BDE in another H-donor, 9,10-dihydrophenanthrene, should be close to the value for 1,3-cyclohexadiene. The reported difference is more than 10 kcal mol⁻¹ (84.6 kcal mol⁻¹ for 9,10-dihydrophenanthrene⁴ and 73.2 kcal mol⁻¹ for 1,3-cyclohexadiene³⁴), which cannot be justified by conformational changes and suggests that (both) values may be in error. Using a more recently³⁶ determined heat of formation of the dihydrophenanthryl radical, a bond strength of 81 kcal mol⁻¹ can be calculated for 9,10-dihydrophenanthrene. In order to obtain a clearer insight into the relative bond strengths, a number of the BDE values needs to be reevaluated.

The donating potency of tetralin in H-transfer reactions is a measure for its reactivity. Because reverse radical disproportionation type activation energies equal the reaction enthalpy, the ease of hydrogen donation is indicative for the bond strength. Choi and Stock³⁷ determined this potency for tetralin at 400 °C to be about 4.5 times less than that of 9,10-dihydroanthracene. This is more in accord with a bond strength difference of 6–7 kcal mol⁻¹ between tetralin and DHA (it actually indicates a ΔE_a of about 2 kcal mol⁻¹) than a difference of 9 kcal mol⁻¹. In the same study, the reactivity of 9,10-dihydrophenanthrene was found to be slightly higher than that of tetralin, suggesting a somewhat lower bond strength.

Conclusions

The benzylic C-H bond dissociation energy in tetralin was measured to be 82.9 ± 1.2 kcal mol⁻¹, which is lower than the estimated values reported before. This still does not fully explain the high reactivity of tetralin relative to other hydroaromatics.⁵ The assumption that the α -hydrogen bond dissociation energy in tetralin equals that in ethyl benzene cannot be justified on the basis of the results from this study. In the same series of experiments the α -C-H bond strength in THF was found to be 92.1 ± 1.6 kcal mol⁻¹, which is in accordance with literature values.

Competition experiments in photoacoustic calorimetry were found to be a useful tool, reducing the lifetime of the *tert*-butoxyl radicals. A broader range of reactants can thus be studied using PAC, by addition of a well-documented (rate constant and BDE) second reactant.

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- (25) The contribution of β -H abstraction can be assessed as follows: The rate constant for β -H abstraction from THF by the *tert*-butoxyl radical is taken equal to that for abstraction from cyclopentane (k per hydrogen = 8.6×10^4 M⁻¹ s⁻¹)²⁶ to give $k_{2\beta\text{THF}} = 3.4 \times 10^5$ and $k_{2\alpha\text{THF}} = 4.3 \times 10^6$ M⁻¹ s⁻¹. Analogously for tetralin with a global rate constant of 8.3×10^6 M⁻¹ s⁻¹ and a β -H abstraction rate constant equal to that in cyclohexane ($k/H = 8.3 \times 10^4$ M⁻¹ s⁻¹,¹⁸ $k_{2\beta\text{TET}} = 3.3 \times 10^5$ and $k_{2\alpha\text{TET}} = 8.0 \times 10^6$ M⁻¹ s⁻¹).
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