The α-C–H BDE in tetralin

A time-resolved photoacoustic calorimetry study

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Abstract The α-C–H bond dissociation enthalpy (BDE) in
tetralin (1,2,3,4-tetrahydronaphtalene) was determined
using time-resolved photoacoustic calorimetry as
357.6 ± 5.4 kJ mol^{-1}. This value is some 10 kJ mol^{-1}
higher than the only previous experimental determination
but in remarkably good agreement with the α-C–H BDEs
in the structurally related compounds such as 1-butene,
cyclohexene, and ethylbenzene.

Keywords Tetralin · Bond dissociation enthalpy ·
Time-resolved photoacoustic calorimetry · Evans–Polanyi

Introduction

Rate constants for hydrogen abstraction are expected to
increase with decreasing bond strength, according to the
Evans–Polanyi (EP) relationship. This concept was widely
used to explain the reactivity of *tert*-butoxyl radical toward
C–H bonds in a series of hydrocarbons [1]. However,
some important exceptions were noted, namely tetralin

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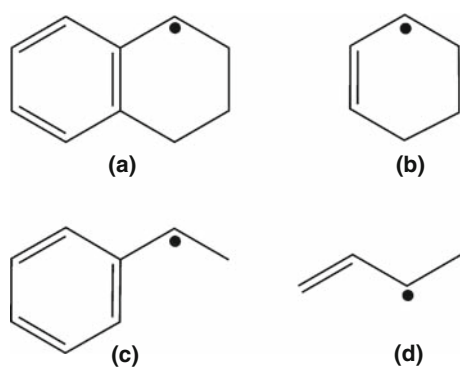Campus de Gambelas, 8005-139 Faro, Portugal

(1,2,3,4-tetrahydronaphtalene, Fig. 1), which motivated an
experimental study by Laarhoven and Mulder leading to a
reevaluation of its α-C–H bond dissociation enthalpy (BDE)
from 356 kJ mol^{-1} (considered equal to that in ethylbenzene
[1], Fig. 1) to 347 kJ mol^{-1} [2]. Yet, as pointed out by the
authors, the new value still did not fully explain the reactivity
of tetralin, and was at odds with equivalent BDEs in similar
compounds. More recently, Finn et al. [3] showed a break-
down of the EP relationship for several substrates, leading to
the conclusion that most hydrogen abstractions from carbon
by *tert*-butoxyl are entropy rather than enthalpy controlled.

Time-resolved photoacoustic calorimetry (TR-PAC) is a
very reliable method to determine BDEs [2, 4]. Using this
technique and high-level quantum chemistry methods, we
recently investigated the C–H BDEs for a series of fun-
damentally important hydrocarbons [5, 6]. Our results
allowed a quantitative description of the observed trends in
terms of hyperconjugation and π-delocalization (in the
radicals), the importance of conjugated double-bonds (in
the parent molecules), and the effect of strain (in both). As
these effects can be rather small in magnitude, this work
demonstrated the need for chemically accurate data (i.e.,
data with uncertainties smaller than ca. 4 kJ mol^{-1}).

In this article, we report our determination of the α-C–H
BDE in tetralin by TR-PAC and discuss the energy–reactivity
relationship of that compound in the light of the more recently
available BDE data for structurally related compounds.

Experimental

Materials

Benzene (Aldrich HPLC grade, 99.9+%) was used without
further purification. Tetralin was washed with small portions

Fig. 1 Radicals produced by hydrogen abstraction from tetralin (**a**) and compounds with similar α-C–H BDEs: cyclohexene (**b**), ethylbenzene (**c**) and 1-butene (**d**)
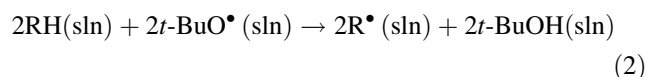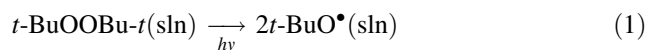
of concentrated H_2SO_4 (until discoloration of the acid fraction), twice with a 10% aqueous solution of Na_2CO_3 and then with distilled water, dried over anhydrous $MgSO_4$, fractionally distilled over sodium under nitrogen, stored under inert atmosphere, and refrigerated. *Ortho*-hydroxy-benzophenone was recrystallized twice from an ethanol–water mixture. Di-*tert*-butylperoxide was purified according to a literature procedure [7].

Photoacoustic calorimetry

The basis of photoacoustic calorimetry [8, 9], our photoacoustic calorimeter setup [10, 11], and the experimental technique are described in detail elsewhere [10, 12]. Briefly, argon-purged solutions in benzene of ca. 0.4 M di-*tert*-butylperoxide and tetralin with concentrations in the range of 0.17 to 0.48 M were flowed through a quartz flow cell (Hellma 174-QS) and photolyzed with pulses from a nitrogen laser (337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral density filters (ca. 10–50 μJ/pulse at the cell). Each laser pulse triggered a photochemical process (see below) that induced a sudden volume change in solution, which generated an acoustic wave, detected by a piezo-electric transducer (0.5 MHz) in contact with the bottom of the cell. The signals were amplified and measured by a digital oscilloscope. The signal-to-noise ratio was improved by averaging 32 acquisitions for each data point obtained at a given laser energy. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched solution of *ortho*-hydroxybenzophenone (in the same mixtures but without the peroxide), which dissipates all of the absorbed energy as heat [8]. For each run (experiment or calibration), four data points were collected corresponding to four different laser intensities obtained using the neutral density filters. The resulting waveforms from each data point were recorded for

subsequent mathematical analysis, affording two waveforms for each point: sample and calibration. The analysis involved, for each laser energy, first the normalization of both waveforms and then the deconvolution of the sample waveform with the calibration waveform [13] using the software Sound Analysis [14].

The photochemical process triggered by the laser pulse was the photolysis of di-*tert*-butylperoxide (*t*-BuOOBu-*t*) generating *tert*-butoxyl radicals, reaction 1, which in turn abstracted the α-C–hydrogen from tetralin, RH, reaction 2.

$$t\text{-BuOOBu-}t(\text{sln}) \xrightarrow[hv]{} 2t\text{-BuO}^\bullet(\text{sln}) \tag{1}$$

$$2RH(\text{sln}) + 2t\text{-BuO}^\bullet(\text{sln}) \rightarrow 2R^\bullet(\text{sln}) + 2t\text{-BuOH}(\text{sln}) \tag{2}$$

Deconvolution of the resulting waveform first allowed to confirm this reaction scheme (reactions 1 and 2) and then afforded the observed fraction of photon energy released as heat, $\phi_{obs,i}$, for each process, and the lifetime of the second, τ_2. An estimate of the rate constant for hydrogen abstraction can be obtained from this lifetime [15].

The enthalpy of reaction 2 was derived from Eq. 3, where $\Delta_{obs}H_2$ corresponds to the observed enthalpy change and is calculated by multiplying $E_m = N_A hv$ (the molar photon energy) by $\phi_{obs,2}$ (the observed heat fraction associated with reaction 2). Φ_r is the reaction quantum yield for the photolysis of di-*tert*-butylperoxide in benzene, 0.83 [16]. All experiments were performed at 300 ± 1 K:

$$\Delta_r H_2 = \frac{-\Delta_{obs}H_2}{\Phi_r}. \tag{3}$$

Results and discussion

The C–H BDE in an organic molecule RH, $DH^o(\text{C–H})$, corresponds to the enthalpy of reaction 4, where all the molecules are in the ideal gas-phase (isolated):

$$RH(g) \rightarrow R^\bullet(g) + H^\bullet(g). \tag{4}$$

Being a solution technique, TR-PAC affords solution-phase BDEs (i.e., all the species in reaction 4 are in solution). To derive the gas-phase BDEs, one needs to consider the solvation enthalpies of all the species in reaction 4, as in Eq. 5. However, in the case of carbon-centered radicals, there is evidence that the solvation enthalpies of $R^\bullet$ and RH are identical (i.e., $\Delta_{sln}H^o(RH,g) \approx \Delta_{sln}H^o(R^\bullet,g)$), and therefore, the solution- and gas-phase BDEs differ only by the solvation enthalpy of the hydrogen atom [4]:

$$DH^o(\text{C–H}) = DH^o_{sln}(\text{C–H}) + \Delta_{sln}H^o(RH,g)$$
$$- \Delta_{sln}H^o(R^\bullet,g) - \Delta_{sln}H^o(H^\bullet,g). \tag{5}$$

From the TR-PAC experiments, we obtained $\Delta_r H_2 = -185.2 \pm 3.0$ kJ mol^{-1} for the enthalpy of reaction 2.[1] As this enthalpy is simply twice the difference between the solution BDEs of the tetralin C–H and *tert*-butyl alcohol O–H, $DH^o_{sln}(C-H)$ can be derived from Eq. 6, where the subscript "sln" indicates that both BDEs are solution values:

$$DH^o_{sln}(C-H) = \Delta_r H_2/2 + DH^o_{sln}(t\text{-BuO}-H). \qquad (6)$$

Our experimental value for $\Delta_r H_2$, coupled with $DH^o_{sln}(t\text{-BuO}-H) = 455.2 \pm 5.2$ kJ mol^{-1} in benzene [4], led to $DH^o_{sln}(C-H) = 362.6 \pm 5.4$ kJ mol^{-1}. Finally, using Eq. 5 with the assumption above $(\Delta_{sln}H^o(RH,g) \approx \Delta_{sln}H^o(R^\bullet,g))$, and $\Delta_{sln}H^o(H^\bullet, g) = 5 \pm 1$ kJ mol^{-1} [17], we obtained 357.6 ± 5.4 kJ mol^{-1} for the gas-phase α-C–H BDE of tetralin.

Besides several estimates [18], the only experimental result for the α-C–H BDE available in the literature is 346.9 ± 5.0 kJ mol^{-1}, obtained from non-time-resolved PAC experiments by Laarhoven and Mulder [2]. However, as reaction 2 with tetralin is very slow, its thermochemistry cannot be easily assessed by non-time-resolved PAC. Therefore, the experiments had to be done either with a high concentration of substrate, or using competing reactions. The authors did both: one set of experiments in neat tetralin and another with a mixture of tetralin and tetrahydrofuran (THF), which yielded concurrent results. We favor the TR-PAC approach because it is less dependent on assumptions [4]. For instance, the derivation of the tetralin BDE in the competition experiments depends on the knowledge of the rate constants for both reactions (*tert*-butoxyl with tetralin and with THF), and of the C–H BDE in THF. TR-PAC directly affords the BDE in tetralin and also provides an estimate for the rate constant of reaction 2: from the lifetime obtained, τ_2, we derived 7×10^6 M^{-1} s^{-1} for the rate constant of hydrogen abstraction from tetralin (k_2), close to the reported laser flash photolysis value of 7.9×10^6 M^{-1} s^{-1} [1]. Finally, our BDE value is in excellent agreement with a result from a preliminary quantum chemistry study using the CBS-QB3 method, viz. 358.9 kJ mol^{-1} [19].

The α-C–H BDE in tetralin can now be compared with C–H BDEs in structurally similar compounds. As pointed out by Laarhoven and Mulder [2], allylic and benzylic resonance stabilization energies should be similar. Nevertheless, the additional factors, e.g., hyperconjugation and strain, should also be considered. And while at the time of that study, the large uncertainties of the available BDEs prevented further elaboration, we have now evidence that

six-membered ring hydrocarbons and their radicals are indeed devoid of strain. Therefore, their BDEs are similar to the corresponding acyclic ones (note, however, that this is no longer true for the five-membered ring hydrocarbons) [6]. In summary, allyl or benzyl radicals, further stabilized by hyperconjugation and devoid of strain (six-membered rings or acyclic), should have BDEs similar to tetralin. The compounds that verify these conditions are, besides tetralin (357.6 ± 5.4 kJ mol^{-1}), 1-butene (359.6 kJ mol^{-1} [5]), cyclohexene (357.9 kJ mol^{-1} [5]), and ethylbenzene (358.8 ± 5.2 kJ mol^{-1} [4]), see Fig. 1. The BDEs are indeed remarkably similar throughout the set.

Finally, it can be stated that our data corroborates the conclusion by Finn et al. [3] regarding the breakdown of the EP relationship for hydrogen abstraction by *tert*-butoxyl radical. For example, our results indicate that the α-C–H BDEs in tetralin and ethylbenzene are similar, meaning that the enhanced reactivity of the former (rate constants for hydrogen abstraction are 7.90×10^6 and 1.05×10^6 M^{-1} s^{-1}, respectively [1]) cannot be explained by its BDE. Nevertheless, those authors did not discard the possibility that some of the BDEs used in their study are in error. A more accurate BDE data set is now being pursued by our group by using a combined approach of TR-PAC and computational chemistry methods.

Conclusions

The α-C–H BDE of tetralin, as determined by TR-PAC, is some 10 kJ mol^{-1} higher than the previous experimental determination, but in excellent agreement with the α-C–H BDEs in structurally similar compounds. This agreement reinforces the view that allylic and benzylic resonance energies are similar and that other important factors to understand the stability of carbon-centered radicals, namely hyperconjugation and strain, were correctly evaluated [5, 6]. Our result also supports Finn et al. [3] conclusion that hydrogen abstractions by *tert*-butoxyl radical in these compounds are entropy controlled.

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[1] The result is the average of seven independent experiments, and the uncertainty is twice the standard deviation of the mean (sdm), according to the thermochemical convention. It is important to note that most authors identify the uncertainty in BDEs with the sdm.

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