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Energetics of the Allyl Group

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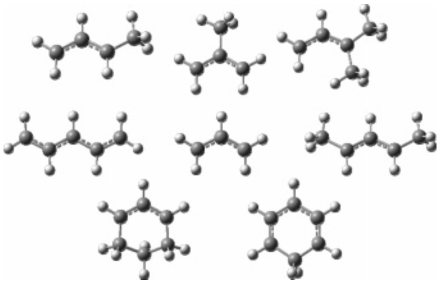

Aiming to improve our understanding of the stability of radicals containing the allylic moiety, carbon−hydrogen bond dissociation enthalpies (BDEs) in propene, isobutene, 1-butene, (*E*)-2-butene, 3-metylbut-1-ene, (*E*)-2-pentene, (*E*)-1,3-pentadiene, 1,4-pentadiene, cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene have been determined by quantum chemistry calculations. The BDEs in cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene have also been obtained by time-resolved photoacoustic calorimetry. The theoretical study involved a DFT method as well as ab initio complete basis-set approaches, including the composite CBS-Q and CBS-QB3 procedures, and basis-set extrapolated coupled-cluster calculations (CCSD(T)). By taking the C(sp^3)−H BDE in propene as a reference, we have concluded that one methyl group bonded to C3 in propene (i.e., 1-butene) leads to a decrease of 12 kJ mol^{-1} and that a second methyl group bonded to C3 (3-methylbut-1-ene) further decreases the BDE by 8 kJ mol^{-1}. When the methyl group is bonded to C2 in propene (isobutene), an increase of 7 kJ mol^{-1} is observed. Finally, a methyl group bonded to C1 in propene (2-butene) has essentially no effect (−1 kJ mol^{-1}). While this trend can be rationalized in terms of stabilization of the corresponding radical (through hyperconjugation and π-delocalization), the BDE values observed for the dienes can only be understood by considering the thermodynamic stabilities of the parent compounds.

Introduction

Bond dissociation enthalpies (BDEs) are fundamental to discuss molecular structure−reactivity relationships. For instance, it has been shown that the antioxidant properties of terpinolene (**1**), α-terpinene (**2**), and γ-terpinene (**3**) are comparable to those of α-tocoferol,[1] without the pro-oxidant effects of this latter compound at higher concentrations.[2] The initial step of the proposed terpene peroxidation mechanism involves hydrogen abstraction by a hydroperoxyl radical.[2] The efficiency of this step will increase with the exothermicity of the abstraction, which in turn corresponds to a decrease of the C−H BDE in the terpene. Therefore, the knowledge of the C−H BDEs in terpenes and other structurally related compounds is of great interest to understand which structural factors influence the antioxidant properties of these compounds.

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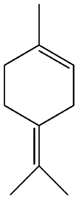
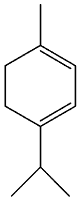


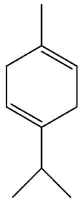
(1)
Terpinolene

(4-isopropylidene-1-methylcyclohexene)



(2)
α-Terpinene

(1-isopropyl-4-methyl-1,3-cyclohexadiene)



(3)
γ-Terpinene

(1-isopropyl-4-methyl-1,4-cyclohexadiene)

The C−H BDE in an organic molecule RH, $DH°(\mathrm{C-H})$, is closely related to the thermodynamic stability of the corresponding carbon-centered radical $\mathrm{R}^\bullet$, as measured by its standard enthalpy of formation $\Delta_f H°(\mathrm{R}^\bullet,\mathrm{g})$. The relation is illustrated by eq 1, the definition of BDE, which corresponds to the enthalpy of reaction 2. Note that all the molecules are in the ideal gas phase (isolated).

$$DH°(\mathrm{C-H}) = \Delta_f H°(\mathrm{R}^\bullet,\mathrm{g}) + \Delta_f H°(\mathrm{H}^\bullet,\mathrm{g}) - \Delta_f H°(\mathrm{RH},\mathrm{g}) \quad (1)$$

$$\mathrm{RH}\ (\mathrm{g}) \rightarrow \mathrm{R}^\bullet\ (\mathrm{g}) + \mathrm{H}^\bullet\ (\mathrm{g}) \quad (2)$$

The stability of a large number of long-lived organic molecules is well established.[3,4] This standard enthalpy of formation database has been very important for the assessment of quantum chemistry methods[5] and has fostered the development of reliable empirical schemes to predict new values.[5−7] The present knowledge on the stability of organic free radicals (as measured by their standard enthalpies of formation or by the corresponding C−H BDEs in their parent molecules, eq 1) is far less satisfactory than that for stable molecules. This is due to the fact that traditional experimental techniques, such as combustion calorimetry, are not suitable to probe the thermochemistry of species whose lifetime is less than ca. 1 μs. Most of the "best" BDEs known for organic compounds have been obtained in the gas phase from kinetics studies, ion cycles, and photoionization mass spectrometry.[8,9] Although these methods may afford chemically accurate results (i.e., with an error smaller than ca. 4 kJ mol^{-1}) this accuracy has only been achieved for a relatively small number of compounds.[8,10] On the other hand, there are abundant examples of large disagreements in literature data for BDEs in many basic compounds.[9,11] For instance, the literature values of α-C−H BDEs in 1,4-cyclohexadiene and in 3-methyl-1-butene span almost 30 kJ mol^{-1}. These uncertainties hinder our understanding of structural effects on C−H BDEs and therefore affect our ability to predict new data.

In this work we report our determinations of C−H BDEs for a series of hydrocarbons containing structural features of terpene molecules. We started our study with the terpenes body, cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene, using time-resolved photoacoustic calorimetry (TR-PAC)[12] and quantum chemistry methods. PAC (and hence TR-PAC) is a very reliable method to determine BDEs.[13] However, unlike the experimental methods referred to above, it is a solution technique (i.e., all the species in reaction 2 are in solution), affording solution-phase BDEs. To derive the gas-phase BDEs, one needs to consider the solvation enthalpies of all the species in reaction 2. For some types of radicals (e.g., oxygen-centered radicals), these data are still a matter of some debate.[14,15] In the case of carbon-centered radicals, there is evidence that the solvation enthalpies of $\mathrm{R}^\bullet$ and RH are identical and therefore the solution- and gas-phase BDEs differ only by the solvation enthalpy of the hydrogen atom.[16] An additional advantage of TR-PAC is that it allows discrimination between competitive reactions, provided that these occur at different rates.

The TR-PAC experimental results were then complemented by quantum chemistry calculations, aiming to understand the effects of the carbon−carbon double bonds and alkyl groups on the C−H BDE. The computational study included the following molecules: propene, isobutene, 1- and (*E*)-2-butene, 3-methylbut-1-ene, (*E*)-2-pentene, (*E*)-1,3- and 1,4-pentadiene, and 1,3- and 1,4-cyclohexadiene. As remarked above, we have found that the accuracy of the literature data for such simple molecules was not sufficient to draw useful conclusions about structural effects on C−H BDEs. On the other hand, a quantitative discussion of the stabilization of the corresponding radical requires only *relative* BDEs. Computational chemistry is a particularly suitable source of these relative data. Their accuracy can in some cases be assessed by using thermochemical cycles that involve well-established enthalpies of formation of parent molecules (RH in reaction 2).

Experimental Section

Materials. Benzene (HPLC grade, 99.9+%) was used without further purification. Cyclohexene (initial purity 99%) was chromatographed in a column of activated alumina grade I under nitrogen and stored in a refrigerator under inert atmosphere. 1,3-Cyclohexadiene (initial purity 97%) was dried over $\mathrm{CaCl_2}$, distilled from $\mathrm{NaBH_4}$ under nitrogen, stored under inert atmosphere, and refrigerated. 1,4-Cyclohexadiene (initial purity 97%) was dried over $\mathrm{CaCl_2}$, distilled under nitrogen, stored in an inert atmosphere, and refrigerated. All three substrates were passed through a column of activated alumina under nitrogen prior to use. Di-*tert*-butyl peroxide was purified according to a literature procedure.[17] *o*-Hydroxybenzophenone was recrystallized twice from an ethanol−water mixture.

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Photoacoustic Calorimetry. The basis of photoacoustic calorimetry,[12,18] our photoacoustic calorimeter setup,[19,20] and the experimental technique are described in detail elsewhere.[21,22] Briefly, argon-purged solutions in benzene of ca. 0.4 M di-*tert*-butyl peroxide and an adequate concentration (see Analysis of Thermochemical Data) of each organic molecule studied (cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene) were flowed through a quartz flow cell and photolyzed with pulses from a nitrogen laser (337.1 nm, pulse width 800 ps). To check for multiphoton effects, the incident laser energy was varied by using neutral density filters (ca. 5−30 μJ/pulse at the cell, flux <40 J m^{-2}). Each pulse produced photolysis of di-*tert*-butyl peroxide (*t*-BuOOBu-*t*), generating *tert*-butoxyl radicals (reaction 3), which in turn abstracted an allylic hydrogen from the organic molecule RH, reaction 4.

$$t\text{-BuOOBu-}t\ (\text{sln}) \xrightarrow{h\nu} 2\ t\text{-BuO}^{\bullet}\ (\text{sln}) \qquad (3)$$

$$2\text{RH}\ (\text{sln}) + 2\ t\text{-BuO}^{\bullet}\ (\text{sln}) \rightarrow 2\text{R}^{\bullet}\ (\text{sln}) + 2\ t\text{-BuOH}\ (\text{sln}) \qquad (4)$$

Each laser pulse induced a sudden volume change in solution, which generated an acoustic wave, detected by a piezoelectric 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 with an optically matched solution of *o*-hydroxybenzophenone (in the same mixtures but without the peroxide), which dissipates all of the absorbed energy as heat.[18] For each run (experiment or calibration), four data points were collected corresponding to four different laser intensities obtained with 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 their deconvolution, using the software Sound Analysis.[23] This analysis first allowed the confirmation of the reaction scheme indicated above (reactions 3 and 4) and then afforded the observed fraction of photon energy released as heat, $\phi_{\text{obs,i}}$, for each process, and the lifetime of the second, τ_2. An estimate of the rate constant can be obtained from this lifetime.[24] The enthalpy of the hydrogen abstraction reaction was derived from eq 5,

$$\Delta_r H_2 = \frac{-\Delta_{\text{obs}} H_2}{\Phi_r} \qquad (5)$$

where $\Delta_{\text{obs}}H_2$ corresponds to the observed enthalpy change and is calculated by multiplying $E_m = N_A h\nu$ (the molar photon energy) by $\phi_{\text{obs},2}$ (the observed heat fraction associated with reaction 2). Φ_r is the reaction quantum yield for the photolysis of di-*tert*-butyl peroxide. All experiments were performed at 293 ± 0.5 K.

Theoretical Calculations. The structures of propene, isobutene, 1- and (*E*)-2-butene, 3-methylbut-1-ene, (*E*)-2-pentene, (*E*)-1,3- and 1,4-pentadiene, cyclohexene, and 1,3- and 1,4-cyclohexadiene, as well as the respective radicals resulting from homolysis of an α-C−H bond, were determined by using density functional theory (DFT).[25] In this approach the energy of a system, $E[\rho]$, is given by eq 6, where V_{NN} is the nucleus−nucleus repulsion energy, H^{core} is the one-electron kinetic and electron-nuclei potential energy contribution to the total energy, and V_{ee} is the Coulombic electron−electron repulsion energy.

$$E[\rho] = V_{\text{NN}} + H^{\text{core}} + V_{\text{ee}} + E_x[\rho] + E_c[\rho] \qquad (6)$$

The terms $E_x[\rho]$ and $E_c[\rho]$ are respectively the exchange and correlation functionals of the electronic density, ρ. The optimized geometry for a molecule is found by determining the set of nuclear coordinates that minimizes the energy given by eq 6. In this work the geometry optimizations were carried out with Becke's three-parameter hybrid method[26] with the correlation functional of Lee, Yang, and Parr (B3LYP).[27] The accuracy of the energy also depends on the completeness of the basis set in which the molecular orbitals are expanded. For these geometry optimizations Dunning's triple-ζ correlation consistent basis set (cc-pVTZ) was used.[28] Vibrational analysis was performed for all optimized geometries to ensure that they represented minima of the energy surfaces. The choice of B3LYP/cc-pVTZ geometries for the structural analysis was dictated by its cost-effectiveness and the fact that several works indicate that the molecular geometries thus obtained are in good agreement with experimental data.[29−31] Nevertheless, it is well-known that DFT methods systematically underestimate bond dissociation enthalpies.[32,33] Therefore, in addition to B3LYP, BDEs were also computed by using two composite theoretical procedures, namely CBS-Q and CBS-QB3.[34−36] These were specifically devised to allow an accurate determination of thermochemical properties for large systems, by resorting to extrapolation to the complete basis set limit. We note, however, that the geometry optimizations of CBS-Q and CBS-QB3 are performed respectively with MP2(FC)/6-31G† (frozen-core Møller−Plesset second-order perturbation theory,[37] in which the electrons from inner shells are excluded from the calculation of the correlation energy) and B3LYP/6-31G†, and therefore are slightly less accurate than B3LYP/cc-pVTZ geometries.[29,31]

Complete basis set extrapolated coupled cluster calculations with single and double excitations and perturbative inclusion of triple excitations (CCSD(T)),[38] using B3LYP/cc-pVTZ geometries, are also reported. Extrapolation of CCSD(T) energies to complete basis set was carried out through a dual (2=cc-pVDZ,3=cc-pVTZ) scheme proposed by Truhlar for both the Hartree−Fock and correlation energies.[39] This procedure has proven to be very reliable for the determination of BDEs,[40,41] although computationally more demanding than any of the aforementioned methods.

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TABLE 1. C−H Bond Dissociation Enthalpies (in kJ mol^{-1}) from the Literature and Determined by Using Theoretical Methods, at 298.15 K

molecule	radical	lit.[a]	CBS-Q[b]	CBS-QB3[b]	B3LYP[b,c]	CCSD(T)[d]
propene	allyl	371.5 ± 1.7[e]	361.3[f]	364.9[f]	352.2	371.5[f]
isobutene	2-methylallyl	360.7 ± 4.2; 372.8	366.9 [377.1]	371.3 [377.9]	359.2 [378.6]	378.2
1-butene	1-methylallyl	341.0 ± 6.3; 350.6	347.8 [358.1]	351.9 [358.5]	334.9 [354.2]	359.6
(*E*)-2-butene	1-methylallyl		360.4 [370.7]	363.1 [369.7]	349.4 [368.7]	370.8
3-methylbut-1-ene	3-methyl-1-buten-3-yl	322.1 ± 6.3;[g] 347.7	340.1 [350.3]	343.8 [350.4]	322.8 [342.1]	351.7
(*E*)-2-pentene	2-penten-4-yl		344.9 [355.2]	351.7 [358.3]	334.0 [353.3]	360.0
(*E*)-1,3-pentadiene	pentadienyl	333.5 ± 4.2; 347.3 ± 12.6	333.5 [343.7]	338.3 [344.9]	326.9 [346.2]	352.5
1,4-pentadiene	pentadienyl	319.7; 332.6 ± 7.1	301.9 [312.1]	310.5 [317.2]	291.9 [311.2]	325.0
cyclohexene	cyclohexen-3-yl	343 ± 10[h]	347.2 [357.5]	349.5 [356.1]	333.8 [353.2]	357.9
1,3-cyclohexadiene	cyclohexadienyl		305.8 [316.1]	311.3 [317.9]	296.4 [315.7]	325.3
1,4-cyclohexadiene	cyclohexadienyl	292.9; 322.2	307.8 [318.0]	311.0 [317.6]	297.0 [316.4]	326.3

[a] Interval of available experimental values quoted from ref 9 (see text), unless noted otherwise. The TR-PAC values determined in the present work are given in the text. [b] Results from the direct homolysis (reaction 2) and from the isodesmic and isogyric reaction (reaction 9 with R′ = allyl and using the experimental C(sp^3)−H BDE in propene, 371.5 kJ mol^{-1}). The later values are bracketed. [c] Calculations performed with Dunning's cc-pVTZ basis set. [d] Complete basis set extrapolated results based on the dual (2,3) scheme proposed by Truhlar (see text). In this case there is no need to derive the BDEs from reaction 9 since the computed C(sp^3)−H BDE in propene matches the experimental result. [e] Selected experimental value, from ref 8. [f] From ref 41. [g] From ref 48. [h] The uncertainty was estimated.

The ground state enthalpies of each parent molecule and radical were calculated from eq 7,

$$H = U + k_BT = E_{\mathrm{elec}} + E_{\mathrm{thermal}} + k_BT \tag{7}$$

where U is the internal energy, E_{elec} is the computed electronic energy, E_{thermal} is the thermal correction to the internal energy at T = 298.15 K (which is calculated from the partition function for each species and includes the zero-point energy correction), and k_B is the Boltzmann constant. For a C−H bond homolysis reaction (eq 2) the reaction enthalpy $\Delta_rH°$, identified with the R−H bond dissociation enthalpy, was computed from eq 8.

$$\Delta_rH° = H(\mathrm{R}^\bullet) + H(\mathrm{H}^\bullet) - H(\mathrm{RH}) \tag{8}$$

The B3LYP/cc-pVTZ calculations were also used to determine the Mulliken atomic spin densities[42−45] for the radical species under study. It is well-known that this population analysis can prove to be unreliable and is, by definition, basis set-dependent. Nonetheless, B3LYP/6-311G** Mulliken spin densities have been successfully used in the study of heterosubstituded allyl radicals.[46] Another factor that led to the choice of this population analysis is the fact that, due to its formal simplicity, it is widely used.

All calculations were carried out with the Gaussian-03 program.[47]

Analysis of Thermochemical Data

We have not attempted to make a comprehensive critical analysis of carbon−hydrogen bond dissociation enthalpies for the molecules investigated in the present study. Instead we have relied mainly on the compilation by Luo,[9] although we have examined in some detail the data collected by this author. This option is enough to provide a clear picture of the available experimental BDE data and to assess their quality.

Table 1 collects literature C−H BDEs for the molecules studied (displayed in Figure 1) and summarizes the values obtained in this work by theoretical methods. Relative BDEs, which provide a clearer picture of BDE trends and are particularly important in discussing the computational data, are presented in Table 2.

Accuracy of Computational Results. As noted in the case of the allyl radical (Table 1), the α-C−H BDEs calculated from eq 8, which relies on reaction 2, are usually low limits of the true values. This problem can be avoided by using isodesmic and isogyric reactions such as

$$\mathrm{RH} + \mathrm{R}'^\bullet \rightarrow \mathrm{R}^\bullet + \mathrm{R}'\mathrm{H} \tag{9}$$

In these reactions the number and type of chemical bonds, the number of carbon atoms in a given state of hybridization, and the number of electron pairs are equal on both sides of the reaction, and therefore advantage is taken from error cancellation.[5] It is also important to ensure that the number of hydrogen atoms bonded to each carbon atom in a given state of hybridization is conserved.[22] If these criteria are met, the differences $DH°(\mathrm{R{-}H}) - DH°(\mathrm{R'{-}H})$, which are equal to the enthalpy of reaction 9, are largely method-independent and usually more accurate than the BDEs obtained from eq 8. Moreover, these differences can then be used to derive absolute BDE values by using a highly reliable value for the anchor, $DH°(\mathrm{R'{-}H})$.

The bracketed values in Table 1 were obtained from reaction 9 with R′ = allyl and using the experimental C(sp^3)−H BDE for propene, 371.5 kJ mol^{-1}. In the case of the 2-methylallyl radical, it is noted that while the BDEs computed from reaction 2 range from 359 to 371 kJ mol^{-1}, the results from reaction 9 agree within 2 kJ mol^{-1}. A similar pattern is observed for the remaining theoretical results in Table 1: the BDEs derived from reaction 9 are much less dependent on the theoretical method than those obtained from the direct homolysis. Analysis of the

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(43) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2343−2346.

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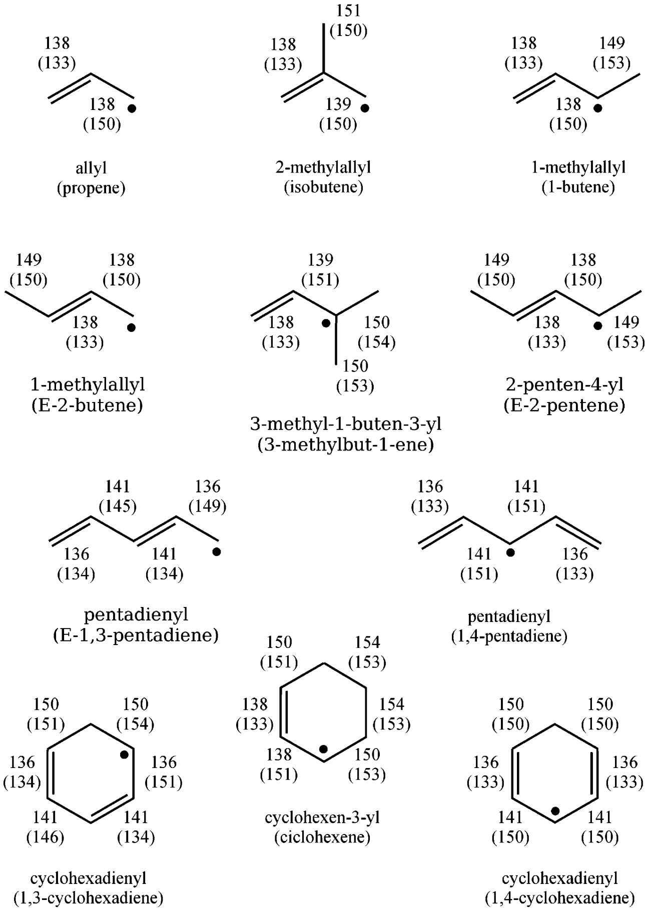

FIGURE 1. Bond lengths (pm) for the radicals and their parent molecules (in parentheses), calculated with B3LYP/cc-pVTZ.

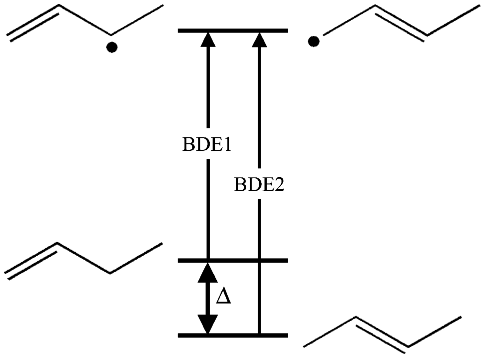

FIGURE 2. Thermochemical cycle relating the C−H bond dissociation enthalpies of 1- and (*E*)-2-butene with their gas-phase standard enthalpies of formation.

DFT and CBS data in Table 1 reveals that the discrepancies between the BDEs obtained from reactions 2 and 9 are smaller for CBS-QB3, which is a strong indication that this is the most accurate of those methods for the systems under study, closely followed by CBS-Q. It is also noted that, apart from CCSD(T) calculations, CBS-QB3 is the one that yields the best value for the C(sp^3)−H BDE in propene.

The CBS-QB3 bracketed values and the data derived from CCSD(T) calculations are in excellent agreement, with the exception of the BDEs for (*E*)-1,3- and 1,4-pentadiene, and 1,3- and 1,4-cyclohexadiene (Table 1). However, even in these cases the discrepancy is smaller than 8 kJ mol^{-1}. In the following discussion we will use the results from these two methods.

(a) Allyl. The enthalpy of formation of the allyl radical seems well established as 173.5 ± 1.8 kJ mol^{-1}, which corresponds to 371.5 ± 1.7 kJ mol^{-1} for the C(sp^3)−H BDE in propene.[8] The CBS-Q and CBS-QB3 results derived from the direct homolysis of the same C−H bond are 361.3 and 364.9 kJ mol^{-1}, respectively. The B3LYP result is even lower, 352.2 kJ mol^{-1}. A CCSD(T) calculation (371.5 kJ mol^{-1}) is in excellent agreement with experiment.[41]

(b) 2-Methylallyl. There are three experimental results for the C(sp^3)−H BDE in isobutene quoted in Luo's compilation,[9] viz. 361 ± 4,[49] 363 ± 3,[50] and 373 kJ mol^{-1}.[51] The first was derived from a pyrolysis study of 2-methyl-1-butene and was in close agreement with the result from a previous shock tube study.[52] Yet, the latter value was recently re-evaluated by its author as 373 kJ mol^{-1}.[51] The second result quoted above (363 ± 3 kJ mol^{-1}) was obtained from a gas-phase kinetic study,[50] which also reported the enthalpy of formation of the allyl radical as 167 ± 3 kJ mol^{-1}, i.e., some 7 kJ mol^{-1} lower than the presently accepted value (see above). This suggests that the best experimental value must be the one recommended by Tsang, 373 kJ mol^{-1}, rather than the one selected by Luo (363 kJ mol^{-1}).[9] Indeed, Tsang's value is closer to the bracketed data in Table 1 and to the result derived from CCSD(T), 378.2 kJ mol^{-1}.

(c) 1-Methylallyl. There are several experimental values for the α-C−H BDE in 1-butene quoted in Luo's compillation,[9] ranging from 341 ± 6 to 351 kJ mol^{-1}. The CBS-QB3 result is 358.5 kJ mol^{-1} (Table 1), in excellent agreement with the one obtained from CCSD(T) (359.6 kJ mol^{-1}), suggesting that the experimental values are low limits.

The C(sp^3)−H BDE in (*E*)-2-butene also leads to the enthalpy of formation of the 1-methylallyl radical. Unfortunately, no experimental values are available. The BDEs derived from CBS-QB3 and CCSD(T) are 369.7 and 370.8 kJ mol^{-1}, respectively (Table 1).

It is very important to note that the computed BDEs for 1- and (*E*)-2-butene are thermodynamically consistent. This can be demonstrated by taking the enthalpies of formation of the respective parent molecules, as shown in Figure 2. The quantity Δ can be calculated as 11.2 kJ mol^{-1} (CBS-QB3 and CCSD(T)) from the difference BDE2 − BDE1. This is in remarkable agreement with 11.3 kJ mol^{-1}, the result obtained from the difference between the experimental enthalpies of formation of 1-butene (−0.1 ± 0.9 kJ mol^{-1}) and (*E*)-2-butene (−11.4 ± 1.0 kJ mol^{-1}).[4]

(d) 3-Methyl-1-buten-3-yl. The available experimental values for the α-C−H BDE in 3-methylbut-1-ene range from 322 to 348 kJ mol^{-1}.[9,48,53,54] The CBS-QB3 and CCSD(T) results are

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(53) Trenwith, A. B. *J. Chem. Soc., Faraday Trans. I* **1982**, *78*, 3131−3136.

(54) Luo incorrectly quotes a lower value of 319.7 kJ mol^{-1}, which in fact corresponds to the C(sp^3)−H BDE in 1,4-pentadiene determined by Trenwith (ref 53). The value for 3-methylbut-1-ene was determined in a previous work by the same author (ref 48).

TABLE 2. Computed α-C−H Bond Dissociation Enthalpies (in kJ mol^{-1}) *Relative* to the C(sp^3)−H BDE in Propene Using the Data Corresponding to the Direct Homolysis Reaction from Table 1

molecule	radical	CBS-Q	CBS-QB3	B3LYP	CCSD(T)
propene	allyl	0.0	0.0	0.0	0.0
isobutene	2-methylallyl	5.6	6.4	7.0	6.7
1-butene	1-methylallyl	−13.5	−13.0	−17.3	−11.9
(*E*)-2-butene	1-methylallyl	−0.9	−1.8	−2.8	−0.7
3-methylbut-1-ene	3-methyl-1-buten-3-yl	−21.2	−21.1	−29.4	−19.8
(*E*)-2-pentene	2-penten-4-yl	−16.3	−13.2	−18.2	−11.5
(*E*)-1,3-pentadiene	pentadienyl	−27.8	−26.6	−25.3	−19.0
1,4-pentadiene	pentadienyl	−59.4	−54.4	−60.3	−46.5
cyclohexene	cyclohexen-3-yl	−14.0	−15.4	−18.4	−13.6
1,3-cyclohexadiene	cyclohexadienyl	−55.5	−53.6	−55.8	−46.2
1,4-cyclohexadiene	cyclohexadienyl	−53.5	−53.9	−55.2	−45.2

350.4 and 351.7 kJ mol^{-1}, respectively (Table 1), i.e., some 18 kJ mol^{-1} higher than the selection by Luo.[9] However, they are close to the value recommended by Brocks et al., 348 kJ mol^{-1}.[55]

(e) 2-Penten-4-yl. The α-C−H BDE in (*E*)-2-pentene, obtained by CBS-QB3, is 358.3 kJ mol^{-1}. To our knowledge there are no experimental values for this BDE.

(f) Pentadienyl. The C(sp^3)−H BDE in (*E*)-1,3-pentadiene ranges from 334 to 347 kJ mol^{-1}.[9] The upper limit, selected by Luo, was recommended in McMillen and Golden's review,[11] and is in good agreement with the CBS-QB3 result, 344.9 kJ mol^{-1}. However, in this case the result derived from CCSD(T) (352.5 kJ mol^{-1}) is some 8 kJ mol^{-1} higher than the CBS-QB3 value (Table 1).

The same radical is also produced by cleaving the C(sp^3)−H bond in 1,4-pentadiene. The corresponding BDE ranges from 320 to 333 kJ mol^{-1}.[9,56] Luo's selection, 321 kJ mol^{-1}, is close to the CBS-QB3 value, 317.2 kJ mol^{-1}. As for the 1,3 isomer, the result derived from CCSD(T) (325.0 kJ mol^{-1}) is 8 kJ mol^{-1} higher than the CBS-QB3 value (Table 1).[57]

As in the case of 1-methylallyl, the thermodynamic consistency of the BDEs for (*E*)-1,3- and 1,4-pentadiene can be assessed by using the experimental enthalpies of formation of the respective parent molecules (Figure 3). The quantity Δ can be calculated as 27.7 (CBS-QB3) or 27.5 kJ mol^{-1} (CCSD(T)) from the difference BDE2 − BDE1. This is in good agreement with the Δ value of 29.6 kJ mol^{-1}computed from the difference between the enthalpies of formation of 1,4-pentadiene (105.7 ± 1.1 kJ mol^{-1}) and (*E*)-1,3-pentadiene (76.1 ± 0.8 kJ mol^{-1}).[4]

(g) Cyclohexen-3-yl. The only experimental result for α-C−H BDE available in the literature and quoted by Luo is 343 kJ mol^{-1}. This value was determined through an electrochemical cycle by Bordwell and co-workers and its uncertainty is no less than 10 kJ mol^{-1}.[58]

TR-PAC experiments in our laboratory led to 349.8 ± 5.6 kJ mol^{-1} for the same BDE. These experiments were performed with cyclohexene concentrations ranging from 0.25 to 0.56 M. From the lifetime obtained for reaction 4, τ_2, we derived 5 × 10^6 M^{-1} s^{-1} for the rate constant of hydrogen abstraction from cyclohexene (k_2), which is in good agreement with a reported laser flash photolysis value, 5.8 × 10^6 M^{-1} s^{-1}.[59]

Both the TR-PAC result and the BDE computed from CBS-QB3 (356.1 kJ mol^{-1}) are higher than the electrochemical value but in keeping with the complete basis set extrapolated CCSD(T) result, 357.9 kJ mol^{-1}.

(h) Cyclohexadienyl. The literature values for C(sp^3)−H BDE in 1,3-cyclohexadiene vary in a narrow range, viz., 305 to 311 kJ mol^{-1}.[9] However, contrary to the information provided by Luo, none of these is a direct experimental result.

It is noted that the CBS-QB3 result (317.9 kJ mol^{-1}) differs by 7 kJ mol^{-1} from the CCSD(T) result (325.3 kJ mol^{-1}). However, the latter is quite close to our TR-PAC value (329.3 ± 5.5 kJ mol^{-1}). In the photoacoustic experiments we used 1,3-cyclohexadiene concentrations ranging from 0.030 to 0.043 M. The lifetime obtained for reaction 4, τ_2, led to a rate constant for the hydrogen abstraction from 1,3-cyclohexadiene of k_2 = 4 × 10^7 M^{-1} s^{-1}. This value is in agreement with a reported laser flash photolysis result, 4.2 × 10^7 M^{-1} s^{-1}.[60]

The cyclohexadienyl radical can also be obtained from 1,4-cyclohexadiene. The literature values for C(sp^3)−H BDE range from 293 to 322 kJ mol^{-1}.[9,61−63] Luo's selection, 318 ± 5 kJ mol^{-1}, relies on a gas-phase kinetic study by Tsang[64] and is in excellent agreement with the CBS-QB3 result, 317.6 kJ mol^{-1}. A BDE value of 312.8 ± 6.1 kJ mol^{-1} was obtained in our laboratory from TR-PAC experiments, which were carried out with 1,4-cyclohexadiene concentrations ranging from 0.032 to 0.036 M. The lifetime calculated for reaction 4, τ_2, led to k_2 = 5 × 10^7 M^{-1} s^{-1} for the rate constant of hydrogen abstraction from 1,4-cyclohexadiene, in agreement with a reported laser flash photolysis value, 5.4 × 10^7 M^{-1} s^{-1}.[60]

In this case, Truhlar's extrapolation of CCSD(T) energies led to 326.3 kJ mol^{-1}, 13 kJ mol^{-1} higher than the experimental TR-PAC value and some 9 kJ mol^{-1} higher than the CBS-QB3 result.

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(55) Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Rüchardt, C. *J. Org. Chem.* **1998**, *63*, 1935−1943.

(56) Clark, K. B.; Culshaw, P. N.; Griller, D.; Lossing, F. P.; Martinho Simões, J. A.; Walton, J. C. *J. Org. Chem.* **1991**, *56*, 5535−5539.

(57) It should be noted that Luo's selection is based on an early PAC result (ref 56) that depended on wrong assumptions and was latter reappraised by Laarhoven et al. (ref 13) as 343.0 kJ mol^{-1}. Although the older value was similar to those obtained through other techniques (namely from appearance energy measurements reported in the same work), Laarhoven et al. considered that the PAC experiment cannot be used to determine this BDE since it is beset by errors resulting from competing reactions.

(58) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229−1231.

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(61) Griller, D.; Wayner, D. D. M. *Pure Appl. Chem.* **1989**, *61*, 717−724.

(62) Ciriano, M. V.; Korth, H. G.; van Scheppingen, W. B.; Mulder, P. *J. Am. Chem. Soc.* **1999**, *121*, 6375−6381.

(63) It should be pointed out that, as in the case of 1,4-pentadiene (see ref 57), the older PAC result (ref 61) quoted by Luo was latter reappraised by Laarhoven et al. (ref 13) and coincides with the most recent PAC value reported in the literature, 322.2 kJ mol^{-1} (ref 62).

(64) Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152−1155.

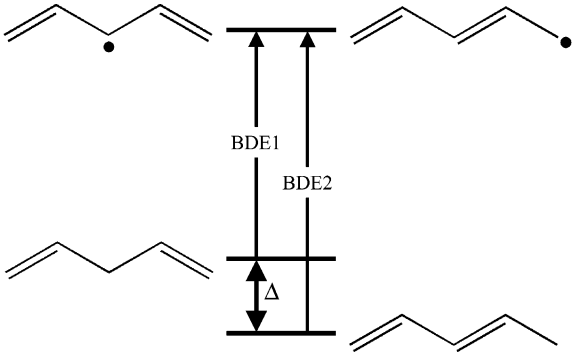

FIGURE 3. Thermochemical cycle relating the C−H bond dissociation enthalpies of (*E*)-1,3- and 1,4-pentadiene with their gas-phase standard enthalpies of formation.

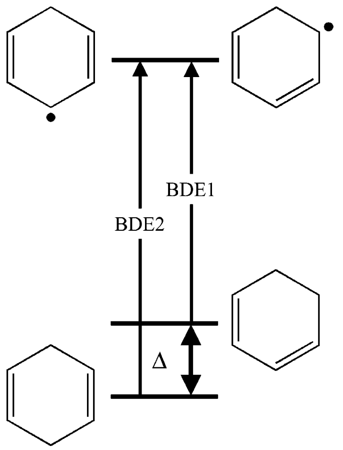

FIGURE 4. Thermochemical cycle relating the C−H bond dissociation enthalpies of 1,3- and 1,4-cyclohexadiene with their gas-phase standard enthalpies of formation.

As discussed for 1-methylallyl and pentadienyl radicals, it is possible to assess the above BDEs through the enthalpies of formation of 1,3- and 1,4-cyclohexadiene (Figure 4). However, this exercise is not as simple as in the previous two cases because there are several discrepant literature values for those enthalpies of formation. Pedley's compillation recommends 106.3 ± 0.9 and 100.4 ± 3.1 kJ mol^{-1} for 1,3- and 1,4-cyclohexadiene, respectively.[4] However, more recent experiments by Steele et al. led to 104.6 ± 0.6 and 104.8 ± 0.6 kJ mol^{-1}.[65] These two pairs of experimental data lead to $\Delta = 5.9 \pm 3.2$ and -0.2 ± 0.8 kJ mol^{-1}, respectively. The TR-PAC results lead to $\Delta = \text{BDE2} - \text{BDE1} = -16.5 \pm 4.4$ kJ mol^{-1}, whereas the theoretical methods imply $\Delta = -0.3$ (CBS-QB3) and 1.0 kJ mol^{-1} (CCSD(T)).

The enthalpies of formation derived by Steele et al. are probably more accurate than the values listed by Pedley. These values imply that 1,3- and 1,4-cyclohexadiene have similar stabilities, which is consistent with both the results from CBS-QB3 and complete basis set extrapolated CCSD(T). We feel therefore inclined to consider that the TR-PAC value is a lower limit. Nevertheless, a reasonable doubt remains: a simple exercise using the extended Laidler terms tabulated by Leal to predict the enthalpies of formation of the isomers[66] leads to $\Delta = -16.4$ kJ mol^{-1}, matching the TR-PAC result.

Hyperconjugation and Resonance Effects

The previous data analysis led to the set of recommended values collected in Table 3. They are all based on the values derived from complete basis set extrapolated CCSD(T) calculations, which in most cases are similar to the CBS-QB3 results. Those values will now be used to discuss the stability of the carbon-centered radicals.

Table 4 displays selected C−H BDEs in methane, ethane, propane, and 2-methylpropane. The BDE trend can be rationalized by using different models. One of these models centers the discussion on the stability of the parent molecules (RH), rather than on the stability of the radicals ($R^{\bullet}$), and claims that the trend is due to a variation of 1,3-repulsive steric interactions (geminal repulsion).[67] This model is able to predict the trend in Table 4 by using an additive scheme and a set of empirical parameters calculated from the enthalpies of formation of the alkanes. Another way to predict the trend in Table 4 is using the electronegativity concept. For instance, Zavitsas' group demonstrated that, in the absence of steric effects, Pauling's equation relating electronegativity to bond dissociation enthalpies yields accurate BDE values.[68] A third model that is often used to explain the trend in Table 4 is focused on the stability of the alkyl radicals, discussed in terms of hyperconjugation.

Hyperconjugation can be described as the radical stabilization due to the overlap between the single-occupied orbital at the carbon atom where the bond dissociation occurred and a neighbor C−H bond σ-orbital. This effect leads to an increase of the electronic density between the two carbon atoms and therefore to a shorter C−C bond.[30] For instance, in the case of the ethyl radical the C−C bond is 4 pm shorter than the corresponding bond in ethane.[30] In the case of the isopropyl radical, our calculations revealed that both C−C bonds are also 4 pm shorter than the C−C bonds in propane, indicating that the radical is stabilized by "double" hyperconjugation.

To discuss the BDE trend in Table 3, we begin by noting that the resonance stabilization of the allyl radical is evaluated as 68 kJ mol^{-1} by comparing the C(sp^3)−H BDE in propene, 371.5 kJ mol^{-1}, with the C−H BDE in methane (Table 4).[69] This resonance effect is reflected by a decrease of the spin density in the carbon atom where the bond dissociation occurred (see below).

The BDE in the allyl radical has been used as the reference for all the remaining BDEs included in Table 3. Therefore, negative values of relative BDEs mean that the corresponding BDE is smaller than the C(sp^3)−H BDE in propene and vice versa. As will be shown below, most of the trends can be understood on the basis of hyperconjugation and resonance. For this purpose, Figure 1 and Table 5 will be used. Figure 1 contains C−C bond lengths in the radicals and their parent molecules, and Table 5 shows Mulliken spin densities in the allylic moiety of each radical. We note that the atomic spin densities for the allyl radical are in good agreement with the experimental and theoretical data reported by Wiberg et al.[46]

(a) 2-Methylallyl. Interestingly, the C(sp^3)−H BDE in isobutene is 7 kJ mol^{-1} higher than the C(sp^3)−H BDE in

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[65] Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. In *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69 (http://webbook.nist-.gov); Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2005.

[66] Leal, J. P. *J. Phys. Chem. Ref. Data* **2006**, *35*, 55−76.

[67] Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209−1219.

[68] Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158−3172.

[69] The comparison should not be made with the C−H BDE in ethane, because the ethyl radical is stabilized by hyperconjugation.

TABLE 3. Selected Values for the Relative, Δ*DH*°(C−H), and Absolute, *DH*°(C−H), α-C−H BDEs (in kJ mol^{-1}), and Recommended Enthalpies of Formation for the Corresponding Radicals[a]

molecule	radical	Δ*DH*°(C−H)	*DH*°(C−H)	$\Delta_f H°(R^•,g)$[b]
propene	allyl	0.0	371.5	173.5
isobutene	2-methylallyl	7	378	143
1-butene	1-methylallyl	−12	360	142
(*E*)-2-butene	1-methylallyl	−1	371	141
3-methylbut-1-ene	3-methyl-1-buten-3-yl	−20	352	106
(*E*)-2-pentene	2-penten-4-yl	−12	360	110
(*E*)-1,3-pentadiene	pentadienyl	−19	353	211
1,4-pentadiene	pentadienyl	−47	325	213
cyclohexene	cyclohexen-3-yl	−14	358	135
1,3-cyclohexadiene	cyclohexadienyl	−46	325	212[c]
1,4-cyclohexadiene	cyclohexadienyl	−45	326	213[c]

[a] Estimated uncertainty of ca. ±4 kJ mol^{-1}. [b] Calculated by using $\Delta_f H°(H^•,g) = 217.998 \pm 0.006$ kJ mol^{-1} (Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *Codata Key Values for Thermodynamics*; Hemisphere: New York, 1989) and $\Delta_f H°(RH,g)$ from ref 4, unless noted otherwise. [c] $\Delta_f H°(RH,g)$ from ref 65.

TABLE 4. Absolute, *DH*°(C−H), and Relative, Δ*DH*°(C−H), BDEs (in kJ mol^{-1}) in Selected Alkanes

molecule	radical	*DH*°(C−H)[a]	Δ*DH*°(C−H)
methane	methyl	439.1 ± 0.5	0.0
ethane	ethyl	423.0 ± 1.7	−16.1
propane	isopropyl	412.5 ± 1.7	−26.6
2-methylpropane	*tert*-butyl	403.8 ± 1.7	−35.3

[a] Data from ref 8, except for methane, which is from ref 10.

TABLE 5. Spin Densities at the Carbon Atoms That Define the Allyl Backbone in the Radicals[a]

molecule	radical	C1	C2	C3
propene	allyl	0.643	−0.210	0.643
isobutene	2-methylallyl	0.669	−0.201	0.617
1-butene	1-methylallyl	0.597	−0.202	0.637
(*E*)-2-butene	1-methylallyl	0.637	−0.202	0.597
3-methylbut-1-ene	3-methyl-1-buten-3-yl	0.575	−0.203	0.624
(*E*)-2-pentene	2-penten-4-yl	0.593	−0.195	0.593
(*E*)-1,3-pentadiene	pentadienyl	0.466	−0.177	0.487
1,4-pentadiene	pentadienyl	0.487	−0.177	0.466
cyclohexene	cyclohexen-3-yl	0.605	−0.197	0.605
1,3-cyclohexadiene	cyclohexadienyl	0.392	−0.160	0.520
1,4-cyclohexadiene	cyclohexadienyl	0.520	−0.160	0.392

[a] C1 is the carbon atom where the bond was cleaved. See Figure 1.

propene. This is in keeping with the data in Table 5: the spin density in the carbon atom where dissociation occurred (C1) is higher than in the case of allyl, indicating a lower electron delocalization. This is probably related to an anisotropy in the electronic distribution induced by the methyl group, which impairs delocalization. Evidence of the anisotropy is provided by the fact that the allylic C−C bond lengths are not equal (Figure 1). It is also suggested by the observation that the shorter allylic C−C bond is coplanar with a C−H bond of the methyl group.

(b) 1-Methylallyl. The α-C−H BDE in 1-butene is 12 kJ mol^{-1} lower than the C(sp^3)−H BDE in propene. Indeed, Table 5 shows that the spin density in C1 is lower than that in allyl, indicating a higher electron delocalization. In addition, it is noted in Figure 1 that the C1−Me bond length in 1-methylallyl is 4 pm shorter than the corresponding bond in 1-butene, suggesting that hyperconjugation is involved.

The 1-methylallyl radical is also formed by cleaving the C(sp^3)−H bond in (*E*)-2-butene. However, as shown in Table 3, the enthalpy of this process is only 1 kJ mol^{-1} lower than the C(sp^3)−H BDE in propene. In other words, producing the 1-methylallyl radical from 1-butene costs 11 kJ mol^{-1} less than producing it from (*E*)-2-butene. The difference, discussed above, stems from the fact that (*E*)-2-butene is 11 kJ mol^{-1} more stable than 1-butene (see Figure 2) and can be rationalized by using the Laidler scheme.[6] Consider the two types of C−C single bonds in 1- and (*E*)-2-butene, by decreasing order of strength (as indicated by bond length data in Figure 1): two C(sp^2)−C(sp^3) bonds in (*E*)-2-butene and one in 1-butene; and one C(sp^3)−C(sp^3) bond in 1-butene. The higher stability of (*E*)-2-butene essentially reflects the difference between the C(sp^2)−C(sp^3) and the C(sp^3)−C(sp^3) bond strengths.

There is an alternative way to explain the 11 kJ mol^{-1} difference between the C−H BDEs in 1-butene and (*E*)-2-butene (see Figure 1). By cleaving a secondary C−H bond in 1-butene the resulting (unrelaxed) fragment is then stabilized by both hyperconjugation and resonance, whereas the fragment formed from (*E*)-2-butene (by cleaving a primary C−H bond) is only stabilized by resonance. In other words, when the C−H bonds in 1-butene and (*E*)-2-butene are cleaved the resulting fragments relax to the ground state of the 1-methylallyl radical, but this relaxation is more exothermic for the fragment formed from 1-butene than that from (*E*)-2-butene.

(c) 3-Methyl-1-buten-3-yl. The α-C−H BDE in 3-methylbut-1-ene is 20 kJ mol^{-1} lower than the C(sp^3)−H BDE in propene. Table 5 indicates a higher degree of delocalization than in the case of allyl. On the other hand, Figure 1 shows that the C1−Me and C1−Me′ in the radical are 3−4 pm shorter than the corresponding bonds in the parent molecule, suggesting "double" hyperconjugation.

(d) 2-Penten-4-yl. The α-C−H BDE in (*E*)-2-pentene is 12 kJ mol^{-1} lower than the C(sp^3)−H BDE in propene. The data in Figure 1 show a shortening of 4 pm in the C1−Me bond (relative to the corresponding bond in the parent molecule), indicating hyperconjugation. Yet, no significant shortening is observed in the C1−C2 bond in (*E*)-2-pentene.

It is interesting to note that the relative C−H BDEs in 1-butene and (*E*)-2-pentene are similar (−12 kJ mol^{-1}). In both cases we have used hyperconjugation to explain this variation. Recall that hyperconjugation was also invoked to justify the C−H BDE in ethane (−16 kJ mol^{-1}), relative to the C−H BDE in methane.

A second comparison is provided by the "double" hyperconjugated 3-methyl-1-buten-3-yl and isopropyl radicals. The relative C−H BDE in 3-methylbut-1-ene (−20 kJ mol^{-1}) can be regarded as the combination of two hyperconjugations, the first of which contributes with −12 kJ mol^{-1} and the second with −8 kJ mol^{-1}. In the case of propane, the relative C−H BDE in propene is −27 kJ mol^{-1} and the individual contributions are −16 and −11 kJ mol^{-1}.

In summary, the hyperconjugation contributions to the stability of alkyl and allyl derivatives are similar. However, they are not equal. The hyperconjugation effect is more important for alkyl radicals than for allyl radicals because in the latter the electron is delocalized and therefore less available to hyperconjugate.

(e) Pentadienyl. The C(sp^3)−H BDE in (*E*)-1,3-pentadiene is 19 kJ mol^{-1} lower than the BDE for the corresponding bond in propene. In both cases the radicals are resonance-stabilized but, as expected, the stabilization is higher in the five-carbon-atom system. This is in keeping with the data in Table 5: the spin density in the carbon atom where dissociation occurred (C1) is lower than that in the case of allyl, indicating a higher electron delocalization.

The pentadienyl radical can also be produced by cleaving the C(sp^3)−H BDE in 1,4-pentadiene, which costs 28 kJ mol^{-1} less than when using the 1,3 isomer as the starting point. As noted in Figure 3, the difference results from the relative stabilities of the isomers, i.e., (*E*)-1,3-pentadiene is about 30 kJ mol^{-1} more stable than 1,4-pentadiene. The existence of conjugated double bonds in the 1,3 isomer, involving a C(sp^2)−C(sp^2) bond, may be responsible for its relative stability, as suggested by the application of a recent set of extended Laidler (bond enthalpy) terms that includes a term for conjugated double bonds.[66] This is consistent with the fact that the conjugated C2−C3 bond in (*E*)-1,3-pentadiene is 6 pm shorter than the C2−C3 or C3−C4 bonds of 1,4-pentadiene (see Figure 1).

(f) Cyclohexen-3-yl. The α-C−H BDE in cyclohexene is 14 kJ mol^{-1} lower than the C(sp^3)−H BDE in propene. This value is similar to the results computed for 1-butene and (*E*)-2-pentene, suggesting that the cyclohexen-3-yl radical is stabilized by hyperconjugation and resonance. The bond length variations in Figure 1 and the spin densities in Table 5, which are comparable to those observed for the 2-penten-4-yl radical, support this conclusion.

(g) Cyclohexadienyl. The α-C−H BDEs in 1,3- and 1,4-cyclohexadiene are about 46 kJ mol^{-1} lower than the C(sp^3)−H BDE in propene. This value could be expected having in mind that the stabilization of pentadienyl and cyclohexadienyl radicals should be similar. The only difference is that (*E*)-1,3-pentadiene is 30 kJ mol^{-1} more stable than the 1,4 isomer, whereas the enthalpies of formation of 1,3- and 1,4-cyclohexadiene are identical.

Understanding the different stabilities of the cyclohexadiene isomers is slightly more complex than in the case of the pentadienes. Consider the three types of C−C single bonds in 1,3- and 1,4-cyclohexadiene, by decreasing order of strength (as indicated by bond length data in Figure 1): one conjugated C(sp^2)−C(sp^2) bond in 1,3-cyclohexadiene; two C(sp^2)−C(sp^3) bonds in 1,3-cyclohexadiene and four in 1,4-cyclohexadiene; and one C(sp^3)−C(sp^3) bond in 1,3-cyclohexadiene. Therefore, the stabilizing effect of the conjugated C(sp^2)−C(sp^2) bond in the 1,3 isomer is apparently offset by a much weaker C(sp^3)−C(sp^3) bond.

Correlation between BDEs and Spin Densities. By plotting the BDEs in Table 3 against the Mulliken atomic spin density at C1 of each radical, a linear correlation is observed (Figure 5). This supports the view that the BDEs are mainly determined by the radical stabilization through electron delocalization. Similar correlations have been reported, for instance, by Brocks et al.,[55] and involved plots of either radical stabilization energies or BDEs against esr-derived hyperfine coupling constants (which can be related to the spin density at the radical center, provided that the radical is planar). An advantage of the correlation in Figure 5 is that spin densities can be directly computed for any radical, regardless of its geometry.

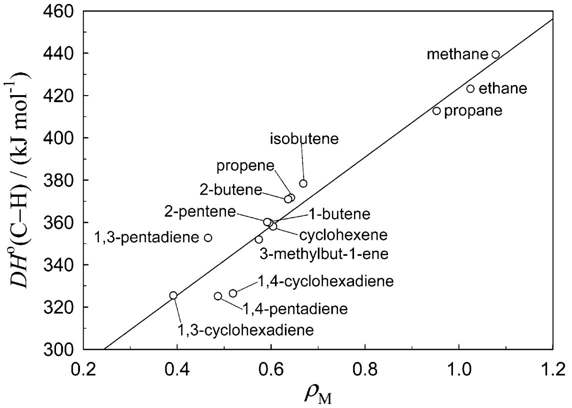

FIGURE 5. C−H bond dissociation enthalpies, ($DH°$(C−H)) vs Mulliken atomic spin densities (ρ_M) at the radical center for selected radicals: $DH°(\text{C−H}) = 163.4\rho_M + 206.3$ ($r = 0.967$).

The plot in Figure 5 (correlation coefficient of 0.967) includes the BDE data in Tables 3 and 4. The correlation fits quite well the values for the alkyl and allyl radicals but not the values for the dienes.

Conclusions

By using quantum chemistry calculations and time-resolved photoacoustic calorimetry, we have attempted to determine carbon−hydrogen bond dissociation enthalpies of selected alkenes within chemical accuracy (ca. 4 kJ mol^{-1}), aiming to improve our understanding of the stability of allylic radicals. By taking the C(sp^3)−H BDE in propene as a reference, we have concluded that one methyl group bonded to C3 in propene (i.e., 1-butene) leads to a decrease of 12 kJ mol^{-1} and that a second methyl group bonded to C3 (3-methylbut-1-ene) further decreases the BDE by 8 kJ mol^{-1}. Interestingly, however, when the methyl group is bonded to C2 in propene (isobutene), an increase of 7 kJ mol^{-1} is observed. Finally, a methyl group bonded to C1 in propene (2-butene) has essentially no effect (−1 kJ mol^{-1}).

The previous conclusions were used to rationalize other relative C−H BDEs. For instance, the α-C−H BDEs in (*E*)-2-pentene and cyclohexene (one alkyl group bonded to C1 and one to C3 in both cases) can be estimated as −13 kJ mol^{-1}, in keeping with the computed results, −12 and −14 kJ mol^{-1}, respectively.

The above values can be rationalized by assuming that the BDE changes are solely due to the stabilization of the corresponding radicals (relative to the stabilization of the allyl radical). In other words, to explain those BDEs (and therefore to predict new data), one does not need to consider the thermodynamic stabilities of the parent compounds. Indeed the relative stabilization of the simple alkenes involved in the present study correlates well with the spin density distribution, indicating that hyperconjugation and π-delocatization can be invoked to understand the BDE trend.

For the dienes, however, the radical-based justification of the BDE trends does not hold, in keeping with the fact that these data do not correlate with the spin density at the radical center (with the probably fortuitous exception of 1,3-cyclohexadiene). The BDE values can only be understood by considering the thermodynamic stabilities of the parent compounds.

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Supporting Information Available: Tables containing computed optimized geometries and total energies for radicals and parent compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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