

Enthalpy of Formation of the Cyclopentadienyl Radical: Photoacoustic Calorimetry and ab Initio Studies

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The gas-phase C–H bond dissociation enthalpy (BDE) in 1,3-cyclopentadiene has been determined by time-resolved photoacoustic calorimetry (TR-PAC) as 358 ± 7 kJ mol⁻¹. Theoretical results from ab initio complete basis-set approaches, including the composite CBS-Q and CBS-QB3 procedures, and basis-set extrapolated coupled-cluster calculations (CCSD(T)) are reported. The CCSD(T) prediction for the C–H BDE of 1,3-cyclopentadiene (353.3 kJ mol⁻¹) is in good agreement with the TR-PAC result. On the basis of the experimental and the theoretical values obtained, we recommend 355 ± 8 kJ mol⁻¹ for the C–H BDE of 1,3-cyclopentadiene and 271 ± 8 kJ mol⁻¹ for the enthalpy of formation of cyclopentadienyl radical.

Introduction

During the last fifty years cyclopentadienyl (C₅H₅) has been widely used as a ligand in organometallic chemistry.^{1–3} Metal–C₅H₅ complexes have been synthesized for all transition and some f-block metals.³ A key value for evaluating metal–cyclopentadienyl bond dissociation enthalpies (BDEs), and thus for discussing the nature of metal–C₅H₅ bonding, is the standard enthalpy of formation of the C₅H₅ radical.^{4–6} An accurate value of $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g})$ is also required to develop kinetic models for the combustion of aromatic compounds.^{7,8}

Surprisingly, the enthalpy of formation of the cyclopentadienyl radical is still subject to controversy. In their 1977 review, Tel'noi and Rabinovich listed several estimates for this quantity, ranging from 190 ± 42 to 264 kJ mol⁻¹.⁵ They have arbitrarily chosen $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 209$ kJ mol⁻¹ to derive a number of metal–C₅H₅ BDEs; in a recent book, by the same group, that value was updated to 237 kJ mol⁻¹.⁹ In 1982, McMillen and Golden recommended $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 242 \pm 6$ kJ mol⁻¹,¹⁰ on the basis of a reassessment of a kinetic study of the iodination of 1,3-cyclopentadiene¹¹ and on a value derived from a proton affinity study of C₅H₅ (264 ± 9 kJ mol⁻¹).¹² This choice was reconfirmed (243 ± 8 kJ mol⁻¹) in a brief analysis of literature data.¹³

Bordwell et al. used a thermodynamic cycle together with the values of pK_a of 1,3-cyclopentadiene and the oxidation potential of C₅H₅⁻, both measured in dimethyl sulfoxide, to derive a value of C₅H₅–H gas-phase BDE consistent with $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 256 \pm 13$ kJ mol⁻¹.^{14,15} Bordwell's group result was later reevaluated by Parker et al.,¹⁶ leading to $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 267 \pm 3$ kJ mol⁻¹. The ca. 11 kJ mol⁻¹ upward correction is

due to a kinetic potential shift caused by the fast dimerization reaction of the oxidation product (cyclopentadienyl), which was not considered in Bordwell's work.

Two other experimental results have appeared more recently, both relying on gas-phase high-temperature kinetics, viz. $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 273$ and 260 ± 4 kJ mol⁻¹.^{8,17} The latter involved the third-law determination of the enthalpy of C₅H₅–H homolysis.⁸

The NIST Chemistry WebBook contains gas-phase ion data from which the C₅H₅–H BDE can be extracted by using thermochemical cycles.¹⁸ One cycle involves the proton affinity of C₅H₅ (831.5 kJ mol⁻¹), the adiabatic ionization energy of 1,3-cyclopentadiene (826.9 ± 1.0 kJ mol⁻¹), and the ionization energy of the hydrogen atom (1312.0 kJ mol⁻¹). This leads to $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 263$ kJ mol⁻¹. The second cycle involves the acidity of 1,3-cyclopentadiene (1481 ± 9 kJ mol⁻¹ or 1485 ± 12 kJ mol⁻¹), the adiabatic electron affinity of C₅H₅ (172.3 ± 1.9 kJ mol⁻¹), and the ionization energy of the hydrogen atom, yielding $\Delta_f H^\circ(\text{C}_5\text{H}_5, \text{g}) = 258 \pm 10$ or 262 ± 12 kJ mol⁻¹.

In summary, the literature values for the standard enthalpy of formation of cyclopentadienyl radical span more than 80 kJ mol⁻¹. Even if only the most recent data are considered (Table 1) the variation is about 30 kJ mol⁻¹. Aiming to improve this situation, we have decided to determine the C₅H₅–H BDE (and the corresponding enthalpy of formation) by using time-resolved photoacoustic calorimetry (TR-PAC) and also quantum chemistry calculations. TR-PAC has been successfully used before to probe the energetics of the benzyl, ethylbenzyl, and cumyl radicals and should provide reliable data for cyclopentadienyl.¹⁹

Experimental Section

Materials. Benzene (Aldrich, HPLC grade, 99.9+%), was used as received. Cyclopentadiene was prepared by cracking dicyclopentadiene (Aldrich, 96%) at 200 °C, distilled using a Vigreux column, collected at 0 °C and used immediately. Di-*tert*-butyl peroxide (Aldrich) was purified according to a

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TABLE 1: Values of the Standard Enthalpy of Formation of Cyclopentadienyl Radical and the Corresponding Gas-Phase C₅H₅-H Bond Dissociation Enthalpy at 298.15 K (Data in kJ mol⁻¹)

authors (year)	method ^a	DH ^o (C ₅ H ₅ -H)	Δ _f H ^o (C ₅ H ₅ [•] ,g)	ref
McMillen & Golden (1982)	Review	326 ± 6 ^b	242 ± 6	10
Bordwell et al. (1988)	EChem	340 ± 13	256 ± 13 ^b	14, 15
Puttemans et al. (1990)	Review	326 ± 9	243 ± 8 ^b	13
Parker et al. (1991)	EChem	351.0 ± 2.1	267.3 ± 2.6 ^b	16
Kern et al. (1998)	GPK	356.9 ^b	273.2	17
Roy et al. (2001)	GPK	343.9 ± 4.2	260.2 ± 4.5 ^b	8
NIST Database (2005)	GPA	341 ± 9	258 ± 10 ^b	18
NIST Database (2005)	GPA	345 ± 12	262 ± 12 ^b	18
NIST Database (2005)	PA	346	263 ^b	18

^a EChem = electrochemical cycle; GPA = gas-phase acidity cycle; GPK = gas-phase kinetics; PA = proton affinity cycle. ^b Calculated using the enthalpy of formation of 1,3-cyclopentadiene from ref 46 (134.3 ± 1.5 kJ mol⁻¹).

literature procedure.²⁰ *ortho*-Hydroxybenzophenone (Aldrich) was recrystallized twice from an ethanol–water mixture.

Photoacoustic Calorimetry. The theoretical basis of time-resolved photoacoustic calorimetry has been widely discussed,^{21,22} and only a brief outline is given here. The TR-PAC technique involves the measurement of an acoustic wave generated by the sudden volume change that occurs when a laser pulse strikes a solution, initiating a sequence of physicochemical processes. The photoacoustic signal thus measured provides information on the intensity and temporal profile of nonradiative energy released during these processes. Using a deconvolution analysis for the time dependence of the signal, both the magnitudes of each of the signal-inducing events and their lifetimes can be determined.²³ The analysis involves first the normalization of the waveform for its respective absorbance and incident laser energy. Extraction of the observed heat fraction, $\phi_{\text{obs},i}$, and the lifetime, τ_i , for each process is then accomplished by the deconvolution of the normalized waveform, facilitated by the use of commercially available software.²⁴ The parameter $\phi_{\text{obs},i}$ is the observed fraction of photon energy released as heat which, when multiplied by the molar energy of the laser photons ($E_m = N_A h\nu$), corresponds to the observed enthalpic change, $\Delta_{\text{obs}}H_i$.

For instance, considering a two step sequential reaction, the enthalpy of the first step (photochemical) and of the second (thermal) are given by eqs 1 and 2, respectively.

$$\Delta_r H_1 = \frac{E_m - \Delta_{\text{obs}}H_1}{\Phi_r} + \frac{\Delta_r V_1}{\chi} \quad (1)$$

$$\Delta_r H_2 = \frac{-\Delta_{\text{obs}}H_2}{\Phi_r} + \frac{\Delta_r V_2}{\chi} \quad (2)$$

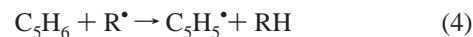
In these equations, Φ_r represents the quantum yield of the first step. As indicated, $\Delta_{\text{obs}}H_i$ are calculated from the respective amplitude $\phi_{\text{obs},i}$ obtained from the deconvolution. Note, however, that $\phi_{\text{obs},i}$ consists not only of a thermal contribution, due to the enthalpy of the reaction but also of a reaction volume contribution, due to the differences between the partial molar volumes of the reactants and products.²⁵ The latter leads to the introduction of a correction factor when calculating the reaction enthalpies. The correction term includes the reaction volume change, $\Delta_r V_i$, and the adiabatic expansion coefficient of the solution, χ . Because the solutions used are usually very diluted, the adiabatic expansion coefficient of the solvent is used as a substitute for the solution value.

Our photoacoustic calorimeter setup and experimental procedure have been described in detail.^{19,26,27} Briefly, benzene solutions of ca. 0.33 M of di-*tert*-butyl peroxide and ca. 0.1 M of 1,3-cyclopentadiene were flowed through a quartz flow cell

(Hellma 174-QS) and photolyzed with pulses from a nitrogen laser (PTI PL 2300, 337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral density filters and the induced acoustic wave was detected by a piezoelectric transducer (Panametrics V101, 0.5 MHz) in contact with the bottom of the cell. The photoacoustic signals were measured by a digital oscilloscope (Tektronix 2430A), where the signal-to-noise ratio was improved by averaging 32 acquisitions. Waveforms were collected at various laser intensities to check for multiphoton effects. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched (within typically 5% absorbance units at 337.1 nm) solution of the photoacoustic calibrant *ortho*-hydroxybenzophenone ($\phi_{\text{obs}} = 1$)²¹ in benzene (this solution does not include the peroxide but contains 1,3-cyclopentadiene, with the same concentration as in the experiment). The sample waveform was deconvoluted with the calibration waveform using the software Sound Analysis by Quantum Northwest.²⁴

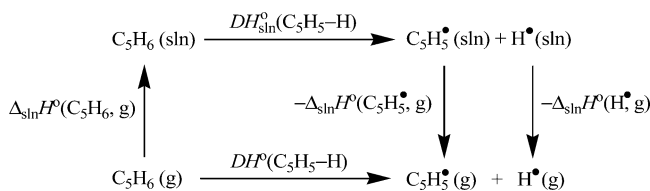
Theoretical Calculations. Different theoretical methods were applied to determine the gas-phase C–H BDE of 1,3-cyclopentadiene, including the complete basis-set composite schemes CBS-Q and CBS-QB3.^{28–30} Further calculations were based on the *ab initio* coupled-cluster method with single and double excitations and perturbative treatment of triple excitations (CCSD(T)).^{31–33} The Dunning's correlation consistent basis sets cc-pVxZ ($x = 2, 3$)^{34–36} were used in coupled-cluster calculations. Initially, optimized geometries and frequencies were determined at the B3LYP/cc-pVTZ level. The choice of this approach was oriented by previous investigations indicating that it is adequate for a reliable prediction of both closed-shell and open-shell structures.³⁷ A dual (2, 3) extrapolation procedure to complete basis-set proposed by Truhlar³⁸ has been applied to CCSD(T) single-point energies using the B3LYP/cc-pVTZ optimized structures. Thermal corrections to 298.15 K were based on B3LYP/cc-pVTZ unscaled frequencies.

The energetics of the bond homolysis reaction 3 and isogyric reactions with methyl, ethyl, allyl, and benzyl radicals (reaction 4, where R = CH₃, CH₃CH₂, CH₂CHCH₂, and C₆H₅CH₂) were studied. In reaction 4, for R = allyl and benzyl, the number of



electron pairs, the number of each type of chemical bond, and the number of carbon atoms in corresponding states of hybridization are all equal in both sides of the chemical equation. Moreover, the number of hydrogen atoms bonded to each carbon atom in a given hybridization is similar in reagents and products. All these factors should contribute to error cancellation. All the

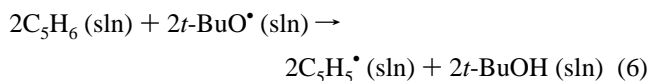
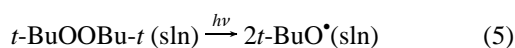
SCHEME 1



calculations were carried out with the Gaussian-03 program and thermal corrections to 298.15 K were applied.³⁹

Results and Discussion

TR-PAC Bond Dissociation Enthalpies. The reactions examined by photoacoustic calorimetry are shown below. A *tert*-butoxyl radical generated from the photolysis of di-*tert*-butylperoxide (reaction 5) in benzene abstracts a hydrogen from the 1,3-cyclopentadiene substrate (C_5H_6), yielding the corresponding cyclopentadienyl radical (reaction 6).



The kinetics of reaction 6 was previously studied using laser flash photolysis and electron paramagnetic resonance techniques.⁴⁰ Although the *tert*-butoxyl radical can also undergo an addition reaction to the C_5H_6 double bonds, it was found that the intensity of the EPR signal from the adduct was hardly detected at temperatures above -20°C . This indicates that the extension of the addition reaction should be negligible at room temperature.

The enthalpy of reaction 6, $\Delta_r H_2$, can be calculated from eq 2 by assuming that the volume change $\Delta_r V_2 \approx 0$, which is sensible because the hydrogen abstraction is a metathesis reaction.⁴¹ Using our experimental value for $\Delta_{\text{obs}} H_2 = 153.3 \pm 7.7 \text{ kJ mol}^{-1}$ and the quantum yield for the photolysis of di-*tert*-butylperoxide in benzene, $\Phi_r = 0.83$,⁴¹ we obtain $\Delta_r H_2 = -184.8 \pm 9.3 \text{ kJ mol}^{-1}$.

$\Delta_r H_2$ is twice the difference between the solution-phase BDEs of $\text{C}_5\text{H}_5\text{-H}$ and *t*-BuO-H, respectively. Therefore, the $\text{C}_5\text{H}_5\text{-H}$ BDE in solution can be calculated using eq 7. Our experimental

$$DH_{\text{sln}}^\circ(\text{C}_5\text{H}_5\text{-H}) = \frac{\Delta_r H_2}{2} + DH_{\text{sln}}^\circ(t\text{-BuO-H}) \quad (7)$$

value for $\Delta_r H_2$ coupled with $DH_{\text{sln}}^\circ(t\text{-BuO-H}) = 455.2 \pm 5.2 \text{ kJ mol}^{-1}$ in benzene,²⁷ led to $DH_{\text{sln}}^\circ(\text{C}_5\text{H}_5\text{-H}) = 362.8 \pm 7.0 \text{ kJ mol}^{-1}$. To calculate the gas-phase value for the $\text{C}_5\text{H}_5\text{-H}$ BDE, we need to consider the solvation enthalpies in Scheme 1. Equation 8 is obtained from this scheme.

$$DH^\circ(\text{C}_5\text{H}_5\text{-H}) = DH_{\text{sln}}^\circ(\text{C}_5\text{H}_5\text{-H}) + \Delta_{\text{sln}}H^\circ(\text{C}_5\text{H}_6, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{H}^\bullet, \text{g}) \quad (8)$$

The difference between the solvation enthalpies of 1,3-cyclopentadiene and the 1,3-cyclopentadienyl radical, $\Delta_{\text{sln}}H^\circ(\text{C}_5\text{H}_6, \text{g}) - \Delta_{\text{sln}}H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g})$ should be negligible.¹⁹ The solvation of the hydrogen atom can be estimated using the hydrogen molecule as a suitable model, yielding $\Delta_{\text{sln}}H^\circ(\text{H}^\bullet, \text{g}) = 5 \pm 1 \text{ kJ mol}^{-1}$ for organic solvents.⁴²⁻⁴⁵ Hence, we obtain $DH^\circ(\text{C}_5\text{H}_5\text{-H}) = 357.8 \pm 7.1 \text{ kJ mol}^{-1}$.

Finally, the standard enthalpy of formation for the $\text{C}_5\text{H}_5^\bullet$ radical in the gas phase was obtained as $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g}) = 274.1 \pm 7.3 \text{ kJ mol}^{-1}$, by using $\Delta_f H^\circ(\text{C}_5\text{H}_6, \text{g}) = 134.3 \pm 1.5 \text{ kJ mol}^{-1}$ ⁴⁶ and $\Delta_f H^\circ(\text{H}^\bullet, \text{g}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$.⁴⁷

Theoretical Gas-Phase Bond Dissociation Enthalpies. Theoretical enthalpies from homolysis reactions (eq 3), which are identified with the C-H BDEs for methane, ethane, 1-propene, 1,3-cyclopentadiene, and toluene, are displayed in Table 2, together with selected experimental data.^{48,49}

The analysis of Table 2 indicates that, with the exception of the results for methane and ethane, which are accurately predicted, significant deviations from experiment are observed for CBS calculations. For example, the CBS-Q result for the C-H BDE of 1,3-cyclopentadiene is $-11.7 \text{ kJ mol}^{-1}$ below the present experimental determination ($357.8 \pm 7.1 \text{ kJ mol}^{-1}$). A similar trend is observed for propene ($-10.2 \text{ kJ mol}^{-1}$), and toluene ($-15.6 \text{ kJ mol}^{-1}$), indicating that the discrepancies occur mainly when resonance stabilized radicals are formed in the homolysis reaction. CBS-QB3 results are in better agreement with experiment, in particular for the C-H bond homolysis of toluene, which is only 3.6 kJ mol^{-1} above experiment ($375.5 \pm 1.8 \text{ kJ mol}^{-1}$). Yet, the CBS-QB3 result for 1,3-cyclopentadiene is still $-11.9 \text{ kJ mol}^{-1}$ below our experimental result.

The above results could have led us to conclude that the $\text{C}_5\text{H}_5\text{-H}$ BDE derived by TR-PAC might be a high upper limit. However, this is not confirmed by basis-set extrapolated CCSD(T) results. Based on these theoretical calculations, the C-H BDE of 1,3-cyclopentadiene is only 4.4 kJ mol^{-1} below the present experimental value. An interesting discussion on the reliability of CCSD(T) calculations was reported by Dunning.⁵⁰

Also reported in Table 2 (bracketed values) are the CCSD(T)/cc-pVxZ//B3LYP/cc-pVTZ ($x = 2, 3$) results. Two features should be emphasized. First, even calculations with a triple- ζ quality basis-set may exhibit deviations from extrapolated results as large as -7.4 kJ mol^{-1} (see CCSD(T) results for 1,3-cyclopentadiene). The deviations are, in general, above chemical accuracy (ca. 4 kJ mol^{-1}) and illustrate the importance of carrying out extrapolation to complete basis-set. Second, in keeping with previous investigations,⁵¹ theoretical homolytic BDEs predicted by coupled-cluster calculations using the dual (2, 3) extrapolation scheme proposed by Truhlar³⁸ are in very good agreement with experiment.

The results for the enthalpies of isodesmic and isogyric reactions 4 are collected in Table 3. The $\text{C}_5\text{H}_5\text{-H}$ BDE in each case was calculated from eq 9 by using the corresponding experimental C-H BDE (see Table 2).

$$DH^\circ(\text{C}_5\text{H}_5\text{-H}) = \Delta_r H^\circ(4) + DH^\circ(\text{R-H}) \quad (9)$$

The CBS results for $\text{C}_5\text{H}_5\text{-H}$ BDE in Table 3 exhibit some dependence on the choice of R^\bullet , the largest deviations from experiment being observed for radicals that are *not* resonance stabilized. This is in keeping with the data in Table 2, where it is observed that these methods underestimate the enthalpies of homolysis reactions involving the formation of resonance stabilized radicals. Therefore, it is expected that the best estimates for $\text{C}_5\text{H}_5\text{-H}$ BDE, obtained from reaction 4, should be the ones where R^\bullet corresponds to the allyl and benzyl radicals. Indeed, with exception of the CBS-QB3 result for $\text{R}^\bullet = \text{benzyl}$, which leads to a deviation from the present experimental value of $-15.5 \text{ kJ mol}^{-1}$, the theoretical results for $\text{R}^\bullet = \text{allyl}$ or benzyl are close to chemical accuracy (ca. 4 kJ mol^{-1}). It is also observed in Table 3 that the CCSD(T) values show smaller deviations from experiment, even when R^\bullet is the

TABLE 2: Theoretical Carbon–Hydrogen BDEs (kJ mol⁻¹) Predicted from Homolysis Reactions^a

	$DH^\circ(\text{C-H})$			
	CBS-Q	CBS-QB3	CCSD(T)	experimental
CH ₃ -H	439.6 (0.5)	440.9 (1.8)	441.4 ^b (2.3) [418.9; 432.9] ^c	439.1 ± 0.5 ^c
CH ₃ CH ₂ -H	425.5 (2.5)	425.5 (2.5)	426.8 ^b (3.8) [406.6; 419.3] ^c	423.0 ± 1.7 ^e
allyl-H	361.3 (-10.2)	364.9 (-6.6)	371.5 ^b (0) [351.9; 364.7] ^c	371.5 ± 1.7 ^e
C ₅ H ₅ -H	346.1 (-11.7)	345.9 (-11.9)	353.4 ^b (-4.4) [332.4; 346.0] ^c	357.8 ± 7.1 ^f
benzyl-H	359.9 (-15.6)	379.1 (3.6)		375.5 ± 1.8 ^d

^a Values in parentheses are deviations from experimental results. ^b Complete basis-set extrapolated result using the dual (2,3) extrapolation scheme of ref 38. ^c CCSD(T)/cc-pVxZ//B3LYP/cc-pVTZ results for x=2 and 3, respectively. ^d Reference 49. ^e Reference 48. ^f This work.

TABLE 3: Theoretical Results for $\Delta_f H^\circ(4)$ ^a and Carbon–Hydrogen BDE for 1,3-Cyclopentadiene (Data in kJ mol⁻¹)

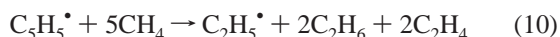
R•	$\Delta_f H^\circ(4)$			$DH^\circ(\text{C}_5\text{H}_5\text{-H})^b$		
	CBS-Q	CBS-QB3	CCSD(T)	CBS-Q	CBS-QB3	CCSD(T) ^c
CH ₃	-93.4	-94.9	-88.0	345.7 (-12.1)	344.2 (-13.6)	351.1 (-6.7)
CH ₃ CH ₂	-79.4	-79.5	-73.4	343.6 (-14.2)	343.5 (-14.3)	349.6 (-8.2)
allyl	-15.1	-18.9	-18.2	356.4 (-1.4)	352.6 (-5.2)	353.3 (-4.5)
benzyl	-13.7	-33.2		361.8 (4.0)	342.3 (-15.5)	

^a C₅H₅-H + R• → C₅H₅• + RH. ^b Values in parentheses are deviations from the present experimental result (357.8 ± 7.1 kJ mol⁻¹). ^c Complete basis-set extrapolated results using the dual (2, 3) scheme of ref 38.

methyl or the ethyl radical. CCSD(T) results for the C–H BDE of 1,3-cyclopentadiene estimated from reaction 3 or 4 when R• = allyl, practically coincide (353 kJ mol⁻¹).

The very good agreement between complete basis-set extrapolated CCSD(T) results and the experimental C–H BDEs for the series of molecules presently investigated, strongly supports the present TR-PAC measurements. However, having in mind the experimental uncertainty and also the best theoretical data in Tables 2 and 3, we recommend a value of 355 ± 8 kJ mol⁻¹ for the C₅H₅-H BDE and $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g}) = 271 \pm 8$ kJ mol⁻¹. These values are in the high range of literature data (Table 1), but in keeping with the data recommended by Parker et al.¹⁶ and Kern et al.¹⁷

The standard enthalpy of formation of the cyclopentadienyl radical has been previously computed as 259.4 kJ mol⁻¹, corresponding to $DH^\circ(\text{C}_5\text{H}_5\text{-H}) = 343.1$ kJ mol⁻¹, by using the G2(B3LYP/MP2,SVP) method for an isodesmic and isogyric reaction with methane (reaction 10).⁷ The 12 kJ mol⁻¹ difference



between that result and our recommended value (355 ± 8 kJ mol⁻¹) is not surprising, because in reaction 10 there is no “resonance conservation”.

To check that the discrepancy was not due to the different calculation methods, we have computed the enthalpy of reaction 10 with CBS-Q, CBS-QB3, and CCSD(T) methods, which led to 172.2, 170.9, and 162.0 kJ mol⁻¹, respectively. From these results and the standard enthalpies of formation of methane (-74.4 ± 0.4 kJ mol⁻¹), ethane (-83.8 ± 0.3 kJ mol⁻¹), ethylene (52.5 ± 0.3 kJ mol⁻¹), and ethyl radical (121.2 ± 1.7 kJ mol⁻¹),^{46,48} $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g})$ can be estimated as 258.4 kJ mol⁻¹ (CBS-Q), 259.7 kJ mol⁻¹ (CBS-QB3), and 268.6 kJ mol⁻¹ (CCSD(T)). The first two estimates are very close to the value derived by Wang and Brezinsky using the G2(B3LYP/MP2,SVP) method (259.4 kJ mol⁻¹).⁷ The CCSD(T) result for $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g})$ derived from reaction 10 (268.6 kJ mol⁻¹) is quite similar to the one based on the homolysis reaction 3, $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g}) = 269.6$ kJ mol⁻¹. Both predictions are only ~2 kJ mol⁻¹ below our recommended value (271 ± 8 kJ mol⁻¹).

Conclusions

Time-resolved photoacoustic calorimetry (TR-PAC) experiments and ab initio calculations (CBS-Q, CBS-QB3, and CCSD-

(T)) were carried out for predicting the gas-phase C–H homolytic bond dissociation enthalpy of 1,3-cyclopentadiene, $DH^\circ(\text{C}_5\text{H}_5\text{-H})$, and the enthalpy of formation of the cyclopentadienyl radical, $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g})$. Our recommended values are $DH^\circ(\text{C}_5\text{H}_5\text{-H}) = 355 \pm 8$ kJ mol⁻¹ and $\Delta_f H^\circ(\text{C}_5\text{H}_5^\bullet, \text{g}) = 271 \pm 8$ kJ mol⁻¹. The best theoretical agreement with experiment is based on complete basis-set CCSD(T) calculations and a simple dual (2,3) energy extrapolation scheme proposed by Truhlar.³⁸

CCSD(T) results for the enthalpies of formation of resonance stabilized radicals are less dependent on the reactions chosen to derive those values (homolysis or isodesmic and isogyric) than the CBS-Q or CBS-QB3 approaches. The CBS methods may lead to significant discrepancies with experiment even when an isodesmic and isogyric reaction is used. To minimize these errors, it is important to “balance” the resonance stabilization of the species in both sides of the reaction.

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