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.⁴ 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.⁴⁻⁵ An accurate value of ΔfH°C₅H₅(g) is also required to develop kinetic models for the combustion of aromatic compounds.⁶⁻⁷

Surprisingly, the enthalpy of formation of the cyclopentadienyl radical is still subject to controversy. In their 1977 review, Tešl'noi and Rabinovich listed several estimates for this quantity, ranging from 190 ± 42 to 264 kJ mol⁻¹.⁸ They have arbitrarily chosen ΔfH°C₅H₅(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 ΔfH°C₅H₅(g) = 242 ± 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 pKa 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 ΔfH°C₅H₅(g) = 256 ± 13 kJ mol⁻¹.¹⁴,¹⁵ Bordwell’s group result was later reevaluated by Parker et al.,¹⁶ leading to ΔfH°C₅H₅(g) = 267 ± 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. ΔfH°C₅H₅(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 ΔfH°C₅H₅(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 ΔfH°C₅H₅(g) = 258 ± 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 \(C_5H_5\) – H Bond Dissociation Enthalpy at 298.15 K (Data in kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Authors (year)</th>
<th>Method(^a)</th>
<th>(\Delta H^\circ(C_5H_5\text{-}H))</th>
<th>(\Delta H^\circ(C_5H_5^*\text{,g}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>McMillen &amp; Golden (1982)</td>
<td>Review</td>
<td>326 ± 6(^b)</td>
<td>242 ± 6</td>
<td>10</td>
</tr>
<tr>
<td>Bordwell et al. (1988)</td>
<td>EChem</td>
<td>326 ± 9</td>
<td>256 ± 8(^b)</td>
<td>14, 15</td>
</tr>
<tr>
<td>Puttermans et al. (1990)</td>
<td>Review</td>
<td>351.0 ± 2.1</td>
<td>267.3 ± 2.6(^b)</td>
<td>13</td>
</tr>
<tr>
<td>Parker et al. (1991)</td>
<td>EChem</td>
<td>356.9(^b)</td>
<td>273.2</td>
<td>16</td>
</tr>
<tr>
<td>Kern et al. (1998)</td>
<td>GPK</td>
<td>343.9 ± 4.2</td>
<td>260.2 ± 4.5(^b)</td>
<td>8</td>
</tr>
<tr>
<td>Roy et al. (2001)</td>
<td>GPK</td>
<td>341 ± 9</td>
<td>258 ± 10(^b)</td>
<td>18</td>
</tr>
<tr>
<td>NIST Database (2005)</td>
<td>GPA</td>
<td>345 ± 12</td>
<td>262 ± 12(^b)</td>
<td>18</td>
</tr>
<tr>
<td>NIST Database (2005)</td>
<td>GPA</td>
<td>346</td>
<td>263(^b)</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\) 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\(^{-1}\)).

The enthalpy of formation of the cyclopentadienyl radical can be determined. The analysis involves first the magnitudes of each of the signal-inducing events and their energy released during these processes. Using a deconvolution procedure, information on the intensity and temporal profile of nonradiative pulse strikes a solution, initiating a sequence of physicochemical changes,23 which, when multiplied by the molar energy of the laser photons (incident laser energy), leads to the extraction of the observed heat fraction, \(\phi_{\text{obs}}\), and the lifetime, \(\tau\), for each process. The analysis involves first the normalization of the waveform for its respective absorbance and incident laser energy. 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.

\[
\Delta H_1 = \frac{E_m - \phi_{\text{obs}}H_1}{\Phi_1} + \frac{\Delta V_1}{\chi} \quad (1)
\]

\[
\Delta H_2 = -\frac{\phi_{\text{obs}}H_2}{\Phi_1} + \frac{\Delta V_2}{\chi} \quad (2)
\]

In these equations, \(\Phi_1\) represents the quantum yield of the first step. \(\Delta_\text{obs}H_i\) are calculated from the respective amplitude \(\phi_{\text{obs}}\), obtained from the deconvolution. Note, however, that \(\phi_{\text{obs}}\) 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. The latter leads to the introduction of a correction factor when calculating the reaction enthalpies. The correction term includes the reaction volume change, \(\Delta V_i\), and the adiabatic expansion coefficient of the solution, \(\chi\). 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. 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 opticaly matched (within typically 5% absorbance units at 337.1 nm) solution of the photoacoustic calibrant ortho-hydroxybenzophenone (\(\phi_{\text{obs}} = 1\))\(^{21\text{b}}\) 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.\(^{24\text{a}}\)

**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-QB.\(^{28\text{a,b,c}, 30\text{a,b}}\) Further calculations were based on the ab initio coupled-cluster method with single and double excitations and perturbative treatment of triple excitations (CCSD(T)). The Dunning’s correlation consistent basis sets cc-pV\(\alpha\)Z\(\alpha\) (\(\alpha = 2, 3\))\(^{31\text{a,b,c}, 32\text{a,b}}\) were used in coupled-cluster calculations. Initially, optimized geometries and frequencies were determined at the B3LYP/cc-pV\(\alpha\)Z\(\alpha\) 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.\(^{33\text{a,b}}\) A dual (2, 3) extrapolation procedure to complete basis-set proposed by Truhlar\(^{34\text{a,b,c}}\) 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 isogyrlic reactions with methyl, ethyl, allyl, and benzy radicals (reaction 4, where \(R = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}(_2\text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2)\) were studied. In reaction 4, for \(R = \text{allyl and benzy}, \) 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

\[
\text{C}_2\text{H}_6 + R^+ \rightarrow \text{C}_3\text{H}_5^* + \text{RH} \quad (4)
\]
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\(_5\)H\(_6\)), yielding the corresponding cyclopentadienyl radical (reaction 6).

\[
\begin{align*}
\text{t-BuOOBu-t (sln)} & \xrightarrow{hv} 2\text{t-BuO}^-(\text{sln}) \\
2\text{C}_2\text{H}_6 (\text{sln}) + 2\text{t-BuO}^- & \rightarrow 2\text{C}_2\text{H}_5^- (\text{sln}) + 2\text{t-BuOH (sln)}
\end{align*}
\] (5) (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\(_2\)H\(_6\) double bonds, it was found that the intensity of the EPR signal from the adduct was hardly detected at temperatures above \(-20^\circ\)C. This indicates that the extension of the addition reaction should be negligible at room temperature.

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

\(\Delta H_2\) is twice the difference between the solution-phase BDEs of C\(_2\)H\(_6\)-H and t-BuO-H, respectively. Therefore, the C\(_2\)H\(_6\)-H BDE in solution can be calculated using eq 7. Our experimental

\[
\Delta H_2 = \frac{1}{2} \Delta_{\text{ash}}H_2 + \Delta_{\text{ash}}H_2 (t\text{-BuO}^- - \text{H})
\]

value for \(\Delta H_2\) coupled with \(\Delta_{\text{ash}}H_2 (t\text{-BuO}^- - \text{H}) = 455.2 \pm 5.2\) kJ mol\(^{-1}\) in benzene,\(^{27}\) led to \(\Delta_{\text{ash}}H_2 (C_2H_6 - H) = 362.8 \pm 7.0\) kJ mol\(^{-1}\). To calculate the gas-phase value for the C\(_2\)H\(_6\)-H BDE, we need to consider the solvation enthalpies in Scheme 1. Equation 8 is obtained from this scheme.

\[
\text{DH}^o_{\text{sig}}(C_2H_5^- - H) = \frac{\Delta H_2}{2} + \Delta_{\text{ash}}H_2 (t\text{-BuO}^- - \text{H})
\]

Finally, the standard enthalpy of formation for the C\(_5\)H\(_5\) radical in the gas phase was obtained as \(\Delta_{\text{sig}}H^o(C_5H_5^* , g) = 274.1 \pm 7.3\) kJ mol\(^{-1}\), by using \(\Delta_{\text{sig}}H^o(C_2H_6, g) = 134.3 \pm 1.5\) kJ mol\(^{-1}\)\(^{46}\) and \(\Delta_{\text{sig}}H^o(H, g) = 217.998 \pm 0.006\) 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-propane, 1,3-cyclopentadiene, and toluene, are displayed in Table 2, together with selected experimental data.\(^{38,49}\)

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 \(-11.7\) kJ mol\(^{-1}\) below the present experimental determination (357.8 \pm 7.1 kJ mol\(^{-1}\)\(^{48}\)). A similar trend is observed for propene (\(-10.2\) kJ mol\(^{-1}\)), and toluene (\(-15.6\) 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 kJ mol\(^{-1}\)). Yet, the CBS-QB3 result for 1,3-cyclopentadiene is still \(-11.9\) kJ mol\(^{-1}\) below our experimental result.

The above results could have led us to conclude that the C\(_2\)H\(_6\)-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-\(\zeta\) 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 Truhlar\(^{38}\) are in very good agreement with experiment.

The results for the enthalpies of isodesmic and isogyric reactions 4 are collected in Table 3. The C\(_2\)H\(_6\)-H BDE in each case was calculated from eq 9 by using the corresponding experimental C-H BDE (see Table 2).

\[
\text{DH}^o(C_2H_6 - H) = \Delta_{\text{sig}}H^o(4) + \text{DH}^o(R - H)
\]

The CBS results for C\(_2\)H\(_6\)-H BDE in Table 3 exhibit some dependence on the choice of R*, 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 C\(_2\)H\(_6\)-H BDE, obtained from reaction 4, should be the ones where R* corresponds to the allyl and benzyl radicals. Indeed, with exception of the CBS-QB3 result for R* = benzyl, which leads to a deviation from the present experimental value of \(-15.5\) kJ mol\(^{-1}\), the theoretical results for R* = 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* is the
TABLE 2: Theoretical Carbon–Hydrogen BDEs (kJ mol\(^{-1}\)) Predicted from Homolysis Reactions\(^a\)

<table>
<thead>
<tr>
<th>R</th>
<th>CBS-Q</th>
<th>CBS-QB3</th>
<th>CCSD(T)</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3), H</td>
<td>439.6 (0.5)</td>
<td>440.9 (1.8)</td>
<td>441.4 (0.3)</td>
<td>439.1 ± 0.5(^c)</td>
</tr>
<tr>
<td>CH(_2)CH(_3), H</td>
<td>425.5 (2.5)</td>
<td>425.5 (2.5)</td>
<td>426.8 (3.8)</td>
<td>423.0 ± 1.7(^c)</td>
</tr>
<tr>
<td>allyl–H</td>
<td>361.3 (10–2)</td>
<td>364.9 (6–6)</td>
<td>371.5 (0)</td>
<td>371.5 ± 1.7(^c)</td>
</tr>
<tr>
<td>C(_5)H(_5)–H</td>
<td>346.1 (11–2)</td>
<td>345.9 (11–9)</td>
<td>353.4 (9–4)</td>
<td>357.8 ± 7.1(^c)</td>
</tr>
<tr>
<td>benzyl–H</td>
<td>359.9 (15–6)</td>
<td>379.1 (3.6)</td>
<td>375.5 ± 1.8(^c)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Values in parentheses are deviations from experimental results.

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, 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 C\(_5\)H\(_5\)–H BDE and \(\Delta H^\circ(C_5H_5^*g) = 271 ± 8\) 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 \(\Delta H^\circ(C_5H_5–H) = 343.1\) 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\(^{-1}\))\(^{46,48}\), \(\Delta H^\circ(C_5H_5^*g)\) 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 \(\Delta H^\circ(C_5H_5^*g)\) derived from reaction 10 (268.6 kJ mol\(^{-1}\)) is quite similar to the one based on the homolysis reaction 3, \(\Delta H^\circ(C_5H_5–H) = 269.6\) 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-

References and Notes
