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Thermodynamic Properties of the C₅, C₆, and C₈ n-Alkanes from ab Initio Electronic Structure Theory

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The heats of formation for the n-alkanes C₅H₁₂, C₆H₁₄, and C₈H₁₈ have been calculated using ab initio molecular orbital theory. Coupled-cluster calculations with perturbative triples (CCSD(T)) were employed for the total valence electronic energies. Correlation-consistent basis sets were used, up through the augmented quadruple zeta, to extrapolate to the complete basis set limit. Geometries were optimized at the B3LYP/TZVP and MP2/aug-cc-pVTZ levels. The MP2 geometries were used in the CCSD(T) calculations. Frequencies were determined at the density functional level (B3LYP/TZVP), and scaled zero point energies were calculated from the B3LYP frequencies. Core/valence, scalar relativistic, and spin–orbit corrections were included in an additive fashion to predict the atomization energies. The core/valence corrections are not small, (≈1.1 kcal/mol per carbon unit) and cannot be neglected for chemical accuracy. The calculated ΔH₀ values are -35.0, -40.2, and -50.2 kcal/mol for C₅H₁₂, C₆H₁₄, and C₈H₁₈, respectively, in excellent agreement with the respective experimental values of -35.11 ± 0.19, -39.89 ± 0.19, and -49.90 ± 0.31 kcal/mol. Isodesmic reaction energies are presented for some simple reactions involving C₈H₁₈ and are shown not to be strongly method dependent.

Introduction

The development of combustion models for hydrocarbon fuels requires reliable heats of formation of reactants, products, and intermediates and as much kinetic information as possible about individual reaction steps. The heats of formation of the longer chain alkanes are of real interest in terms of developing models for gasoline and diesel fuel combustion. Although the heats of formation of the alkanes up through the nonanes are reasonably well-established, there is much less known about the heats of formation of higher alkanes, especially the cetanes and other compounds of interest for diesel fuel.1 There is also little reliable information currently available for the heats of formation of many of the radical intermediates of interest in combustion processes. The heats of formation of the C₁₋C₁₆ alkanes have been calculated at the G3 level with different variations.2 The G3 method3 is an additive, ab initio molecular orbital approach that employs a few empirical corrections with good theoretical justification. In their work on the C₁₋C₁₆ alkanes, Redfern et al.2 compared their ab initio molecular orbital (MO) results with density functional theory (DFT) using the B3LYP exchange-correlation functional and found poor agreement for the DFT results with the MO results and the available experimental results.

We have been developing an approach6–18 to reliably calculate molecular thermodynamic properties, notably heats of formation, based on ab initio molecular orbital theory. Our approach is based on calculating the total atomization energy of a molecule and using this energy in combination with known heats of formation of the atoms to calculate the heat of formation at 0 K. This approach starts with coupled-cluster theory, including a perturbative triples correction (CCSD(T)),19–21 combined with the correlation-consistent basis sets22,23 extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core–valence interactions and relativistic effects, both scalar and spin–orbit. Finally, one must include the zero point energy obtained from either experiment or theory, or some combination. The standard heats of formation of compounds at 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor–harmonic oscillator approximation and the appropriate corrections for the heat of formation of the atoms.25

This approach has been used previously to calculate the heats of formation of the small alkanes CH₄, C₂H₆, C₃H₈, and C₄H₁₀.12,14 As part of our effort to develop the models and tools needed to predict the energetics of higher alkanes, we have used this approach to predict the heats of formation of C₅H₁₂, C₆H₁₄, and C₈H₁₈. Our goal is to reliably predict these heats of formation and then to see what approximations can be made to predict the heats of formation of key radicals and of longer chains.

Computational Approach

For the current study, we used the augmented correlation-consistent basis sets aug-cc-pVnZ for H and C (n = D, T, Q).22,23 For the sake of brevity, we abbreviate the names to aVnZ. Only the spherical components (5d, 7f, 9g, and 11h) of the Cartesian basis functions were used. The valence shell correlation energies were calculated at the CCSD(T) level. The CCSD(T) total energies were extrapolated to the CBS (complete basis set) limit.
TABLE 1: Zero Point Energies in kcal/mol

<table>
<thead>
<tr>
<th>method</th>
<th>C3H6</th>
<th>C4H10</th>
<th>C6H14</th>
<th>C8H18</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5Σνr(exp</td>
<td>97.34</td>
<td>114.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5Σωr(B3LYP)</td>
<td>100.30</td>
<td>118.08</td>
<td>153.76</td>
<td></td>
</tr>
<tr>
<td>0.5Σωr(B3LYP)/CH4 scaling</td>
<td>99.22</td>
<td>116.81</td>
<td>152.11</td>
<td></td>
</tr>
<tr>
<td>0.5Σ(0.5Σνr(exp) + 0.5Σωr(B3LYP))</td>
<td>98.99</td>
<td>116.53</td>
<td>151.75</td>
<td></td>
</tr>
</tbody>
</table>

See text for details of scaling procedure.

Five values are given for the ZPE correction in Table 1. The first value is 0.5Σνr, where the νr are the experimental anharmonic frequencies if available. The second value is 0.5Σωr, where ωr are the unscaled B3LYP harmonic frequencies. The third value is the unscaled B3LYP harmonic frequencies scaled by the ratio of the best anharmonic ZPE value14,32 for CH4 divided by the B3LYP value for CH4. The fourth value is the unscaled B3LYP harmonic frequencies scaled by the ratio of the best anharmonic ZPE value14 for CH4 divided by the B3LYP value for C6H10. The fifth value is the average of the experimental and unscaled B3LYP zero point energies. We used the fourth value when calculating atomization energies for the compounds C5H12, C7H14, and C8H18 because C6H10 is a better representative of the longer chain alkanes than CH4. The scaled results using the C6H10 scaling differ by 0.23, 0.28, and 0.36 kcal/mol for C5H12, C7H14, and C8H18, respectively.

Core/valence corrections, ΔECV, were obtained at the CCSD(T)-Fock (ROHF) level of theory.31 Scalar relativistic corrections (ΔESp), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were obtained at the CCSD(T) level with the cc-pVTZ-DK basis set34 and the spin-free, one-electron Douglas–Kroll–Hess (DKH) Hamiltonian.

Most calculations done with available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state. Instead, the energy is a weighted average of the available multiplets. A correction of 0.08 kcal/mol is needed for each C atom, taken from the excitation energies of Moore.

By combining our computed ΣDν values with the known heats of formation57 at 0 K for the elements, ΔHν/2(C) = 169.98 ± 0.1 kcal mol⁻¹ and ΔHν/2(H) = 51.63 kcal mol⁻¹, we can derive ΔHν/2 values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.25

All of the calculations were performed with the NWChem38 suite of programs and Ecce39 (Extensible Computational Chemistry Environment), a problem-solving environment. The calculations were done on a massively parallel HP Linux cluster with Itanium-2 processors. The largest calculation performed was the CCSD(T) calculation on octane with 1468 basis functions (the aug-cc-pVQZ basis set). The perturbative triples (T) for octane took 23 h on 1400 processors, yielding 75% CPU efficiency and a sustained performance of 6.3 TFlops. Fourteen iterations were required for convergence of the CCSD, which took approximately 43 h on 600 processors.

Results and Discussion

We studied the n-alkanes (CnH2n+2) for compounds up to n = 8 (octane). The valence CCSD(T)/CBS total energies are given in Table 2. The total energies at the valence CCSD(T) level as a function of basis set, geometry parameters, and the vibrational frequencies are given as Supporting Information. The various components needed to calculate the total dissociation energy of CnH2n+2 into nC + (2n + 2)H atoms are given in Table 3.

The experimental bond distance40 for CH4 is 1.0870(7) Å, in good agreement with our values. The experimental microwave and infrared geometry41 for C2H6 has r(C–C) = 1.522(2) Å, r(C–H) = 1.089(1) Å, and ∠CHCH = 111.2°, again in excellent agreement with our calculated geometries. Although the gas phase geometries of some of the larger alkanes have been measured by electron diffraction, only an average geometry is usually given.42 Our optimized geometries are in good agreement with the average geometries.

The experimental vibrational frequencies53,44 for the alkanes up to C6H14 are available, and we compared them with our calculated values. The overall agreement is quite reasonable. The calculated zero point energies for C6H12, C7H14, and C8H18 are given in Table 1. For C5H12, the difference between the B3LYP value and the value obtained from ZPE = 0.5Σνr, where the νr are the experimental fundamental transitions, is 3.0 kcal/mol. For C6H12 this difference is 3.7 kcal/mol. Averaging these two values gives a value within 0.3 kcal/mol of the ZPE obtained when using the scaled butane value. It is worth noting that for ±1 kcal/mol accuracy for these moderate-size alkanes we need better than 1% accuracy in the ZPE correction alone, because the zero point energies for even C4H10 are near 100 kcal/mol. For C8H18, we need a higher percentage accuracy in the ZPE correction to maintain our desired level of chemical accuracy. It is useful to note that the zero point energy is just above 6% of the total valence shell energy contribution to the atomization energy.

After the ZPE, the next largest correction to the total atomization energy is the core/valence (CV) correction. These
values are not small, ranging from 5.4 kcal/mol for C₈H₁₂ to 8.6 kcal/mol for C₆H₁₄, and clearly cannot be neglected. The average value per carbon atom for these compounds is 1.08 kcal/mol. In addition to the coupled-cluster CCSD(T) value, we can easily obtain the CV correction at the MP2 level. It is important to see if the MP2 value is close to the CCSD(T) value because, after the CCSD(T)/aug-cc-PVQZ calculation, obtaining the CV corrections with a largest difference of 0.6 kcal/mol. The result for pentane differs by only 0.07 kcal/mol from the experimental value. It is useful to remember that there is a ±0.1 kcal/mol per C atom uncertainty in our heats of formation due to the uncertainty in the heat of formation of the C atom in the gas phase. For octane, the uncertainty in the atomization energy alone due to the uncertainty in \( \Delta H_{0}(C) \) is 0.8 kcal/mol. Our value of \(-50.20 \text{ kcal/mol for } \Delta H_{298}^{\text{exp}}(\text{C}_8 \text{H}_{18})\), octane’s heat of formation, compares favorably to the G3 value of \(-50.74 \text{ kcal/mol}\). The close agreement of our value with the G3 value is interesting in that the G3 method does not include a scalar relativistic correction, which for C₈H₁₈ is \(-2.3 \text{ kcal/mol}\). This suggests that the higher order correction in G3 accounts for such corrections or that other errors are canceling each other in the G3 approach. As noted by Redfern et al.,² conformational averaging, which is more important the larger the chain, will raise our calculated value by 0.5–1 kcal/mol. For example, they calculated corrections due to conformational averaging of 0.26 and 0.46 kcal/mol for \( n \)-C₆H₁₄ and \( n \)-C₈H₁₂, respectively.² Even with the conformational averaging correction, our calculated values would still be in excellent agreement with the experimental values. We note that the calculated 298 K values are in much better agreement with experiment compared to the 0 K values due, in part, to the different treatments of the vibrational corrections between our calculated results and those obtained from the thermodynamic tables.

To calculate the heats of formation of larger alkanes, we can consider other approaches including the use of isodesmic reactions. For example, the reaction energy for the following two isodesmic reactions could be used in a reverse process to calculate the heat of formation of an unknown, for example, a higher alkane:

\[
\begin{align*}
\text{C}_4\text{H}_{10} + \text{C}_8\text{H}_{18} & \rightarrow \text{C}_8\text{H}_{18} + \text{CH}_4 \\
\text{C}_4\text{H}_{10} + \text{C}_8\text{H}_{14} & \rightarrow \text{C}_8\text{H}_{18} + \text{C}_2\text{H}_6
\end{align*}
\]
Heats of formation of C₈H₁₈ are also given in Table 5 based on within 1 kcal/mol for all methods and basis sets. The resulting ΔZPE corrections are approximately additive in terms of electronic and zero point energy effects are small, suggesting that the ΔECV and ΔES₀ contributions are approximately additive in terms of the number of CH₂ groups. For this case, consistent with the known group additive behavior of the alkanes, even the MP2/aug-cc-pVDZ calculations work well for predicting the isodesmic reaction energies.

Conclusions

We have calculated the heats of formation for the n-alkanes C₄H₁₀, C₅H₁₂, and C₆H₁₄ using ab initio molecular orbital theory in an additive approach with no empirical corrections to the electronic energy. The agreement with experiment for our calculated heats of formation is excellent, further demonstrating the utilization of our method for making such predictions.

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Supporting Information Available: Total CCSD(T) and MP2 valence energies as a function of basis set, optimized geometry parameters, and B3LYP/TZVP and experimental vibrational frequencies in Tables SM-1, SM-2, and SM-3. This material is available free of charge via the Internet at http://pubs.acs.org.

### References and Notes


