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Thermodynamic Properties of the C_5, C_6, and C_8 *n*-Alkanes from ab Initio Electronic Structure Theory

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The heats of formation for the *n*-alkanes C_nH_{n+2} for $n = 5$, 6, and 8 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 ΔH_f^{298} values are −35.0, −40.2, and −50.2 kcal/mol for C_5H_{12}, C_6H_{14}, and C_8H_{18}, 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 C_8H_{18} 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 C_1-C_{16} alkanes have been calculated at the G3 level with different variations.[2] The G3 method[3] is an additive, ab initio molecular orbital approach that employs a few empirical corrections with good theoretical justification. In their work on the C_1-C_{16} alkanes, Redfern et al.[2] compared their ab initio molecular orbital (MO) results with density functional theory (DFT) using the B3LYP exchange-correlation functional[4,5] and found poor agreement for the DFT results with the MO results and the available experimental results.

We have been developing an approach[6−18] 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 sets[22,23] 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[24] 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 CH_4, C_2H_6, C_3H_8, and C_4H_{10}.[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 C_5H_{12}, C_6H_{14}, and C_8H_{18}. 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-pV*n*Z for H and C (*n* = D, T, Q).[22,23] For the sake of brevity, we abbreviate the names to aV*n*Z. Only the spherical components (5*d*, 7*f*, 9*g*, and 11*h*) 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

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TABLE 1: Zero Point Energies in kcal/mol[a]

method	C_5H_{12}	C_6H_{14}	C_8H_{18}
$0.5\sum\nu_i$(expt)	97.34	114.35	
$0.5\sum\omega_i$(B3LYP)	100.30	118.08	153.76
$0.5\sum\omega_i$(B3LYP)/CH_4 scaling	99.22	116.81	152.11
$0.5\sum\omega_i$(B3LYP)/C_4H_{10} scaling	98.99	116.53	151.75
$0.5(0.5\sum\nu_i(\text{expt}) + 0.5\sum\omega_i(\text{B3LYP}))$	98.82	116.22	

[a] See text for details of scaling procedure.

by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\text{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \qquad (1)$$

with $n = 2$ (DZ), 3 (TZ), and 4(QZ), as first proposed by Peterson et al.[26] This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment compared to other extrapolation approaches up through $n = 4$. The open shell CCSD(T) calculations for the C atom were performed at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled-cluster calculation.[27−29]

The geometries were optimized at the density functional theory[30] (DFT) level with the B3LYP exchange-correlation functional[4,5] and the TZVP optimized DFT basis set.[31] These geometries were used as input for optimization at the MP2/aug-cc-pVTZ level, and the MP2 geometries were used for the CCSD(T) calculations. Vibrational frequencies were calculated at the B3LYP/TZVP level. To calculate zero point energies, which are not small for these molecules, we need to potentially introduce scaling factors because the calculated vibrational frequencies correspond to harmonic values, and it is necessary to account for anharmonic corrections to the zero point energy (ZPE).

Five values are given for the ZPE correction in Table 1. The first value is $0.5\sum\nu_i$, where the ν_i are the experimental anharmonic frequencies if available. The second value is $0.5\sum\omega_i$, where ω_i are the unscaled B3LYP harmonic frequencies. The third value is the unscaled B3LYP harmonic frequencies scaled by the ratio of the best anharmonic ZPE value[14,32] for CH_4 divided by the B3LYP value for CH_4. The fourth value is the unscaled B3LYP harmonic frequencies scaled by the ratio of the best anharmonic ZPE value[14] for C_4H_{10} divided by the B3LYP value for C_4H_{10}. 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 C_5H_{12}, C_6H_{14}, and C_8H_{18} because C_4H_{10} is a better representative of the longer chain alkanes than CH_4. The scaled results using the C_4H_{10} scaling compared to the use of CH_4 scaling differ by 0.23, 0.28, and 0.36 kcal/mol for C_5H_{12}, C_6H_{14}, and C_8H_{18}, respectively.

Core/valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[33] Scalar relativistic corrections (ΔE_{SR}), 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 set[34] and the spin-free, one-electron Douglas−Kroll−Hess (DKH) Hamiltonian.[35] 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.[36]

TABLE 2: Total CCSD(T) and MP2 Energies (E_h) Extrapolated to the Complete Basis Set Limit

molecule	CCSD(T) energy	MP2 energy
CH_4	−40.457 446	−40.434 752
C_2H_6	−79.711 584	−79.673 276
C_3H_8	−118.969 085	−118.915 813
C_4H_{10}	−158.226 675	−158.158 548
C_5H_{12}	−197.484 333	−197.401 164
C_6H_{14}	−236.742 023	−236.644 829
C_8H_{18}	−315.257 296	−315.129 243

By combining our computed $\sum D_0$ values with the known heats of formation[37] at 0 K for the elements, $\Delta H_f^0(\text{C}) = 169.98 \pm 0.1$ kcal mol^{-1} and $\Delta H_f^0(\text{H}) = 51.63$ kcal mol^{-1}, we can derive ΔH_f^0 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 NWChem[38] suite of programs and Ecce[39] (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 (C_nH_{2n+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 C_nH_{2n+2} into nC + $(2n + 2)$H atoms are given in Table 3.

The experimental bond distance[40] for CH_4 is 1.0870(7) Å, in good agreement with our values. The experimental microwave and infrared geometry[41] for C_2H_6 has $r(\text{C}-\text{C}) = 1.522(2)$ Å, $r(\text{C}-\text{H}) = 1.089(1)$ Å, and $\angle\text{CCH} = 111.2°$, 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 frequencies[43,44] for the alkanes up to C_6H_{14} are available, and we compared them with our calculated values. The overall agreement is quite reasonable. The calculated zero point energies for C_5H_{12}, C_6H_{14}, and C_8H_{18} are given in Table 1. For C_5H_{12}, the difference between the B3LYP value and the value obtained from ZPE $= 0.5\sum\nu_i$, where the ν_i are the experimental fundamental transitions, is 3.0 kcal/mol. For C_6H_{12} 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 C_5H_{12} are near 100 kcal/mol. For C_8H_{18}, 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

TABLE 3: Calculated Energetic Contributions to the Atomization Energies Based on CCSD(T)/CBS at 0 K[a]

molecule	CCSD(T)/CBS[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0(0 K)
CH_4	419.07	27.6	1.12	−0.26	−0.08	392.2
C_2H_6	710.57	45.9	2.17	−0.53	−0.16	666.2
C_3H_8	1004.18	63.6	3.24	−0.80	−0.24	942.8
C_4H_{10}	1297.89	81.4	4.33	−1.06	−0.32	1219.4
C_5H_{12}	1591.55	99.0	5.39	−1.33	−0.40	1496.2
C_6H_{14}	1885.28	116.5	6.47	−1.60	−0.48	1773.2
C_8H_{18}	2472.67	151.8	8.60	−2.28	−0.64	2326.6

[a] Results are given in kcal/mol. The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated to the complete basis set limit by using eq 1 with the avDZ, aVTZ, and aVQZ basis sets. [c] The zero point energies were obtained as described in the text. [d] Core/valence corrections were obtained with the CCSD(T)/cc-pwCVTZ basis sets at the optimized geometries. [e] The scalar relativistic correction is based on a CCSD(T)/cc-pVTZ-DK calculation. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Value of 0.08 for C is based on Moore's tables.[36]

TABLE 4: Calculated Heats of Formation (kcal/mol) Compared to Experiment

	CCSD(T)		expt (ref 1)	
molecule	0 K	298 K	0 K	298 K
CH_4	−15.7	−17.6	−15.92 ± 0.10	−17.81 ± 0.10
C_2H_6	−16.5	−20.3	−16.30 ± 0.07	−20.03 ± 0.07
C_3H_8	−19.8	−25.2	−19.70 ± 0.12	−25.02 ± 0.12
C_4H_{10}	−23.2	−30.1	−23.23 ± 0.14	−30.31 ± 0.14
C_5H_{12}	−26.7	−35.0	−27.46 ± 0.19	−35.11 ± 0.19
C_6H_{14}	−30.4	−40.2	−31.09 ± 0.19	−39.89 ± 0.19
C_8H_{18}	−37.6	−50.2	−38.70 ± 0.31	−49.90 ± 0.31

values are not small, ranging from 5.4 kcal/mol for C_5H_{12} to 8.6 kcal/mol for C_8H_{18}, 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 correction is the next most expensive calculation. The CCSD(T) CV correction is larger than the MP2 value by 0.95 kcal/mol for octane (ΔE_{CV}(MP2) = 7.65 kcal/mol), 0.73 kcal/mol for hexane (ΔE_{CV}(MP2) = 5.74 kcal/mol), and 0.62 for pentane (ΔE_{CV}(MP2) = 7.65 kcal/mol). The difference between the MP2 and CCSD(T) CV corrections is growing with molecular size, and thus, for the larger alkanes ($n > 8$), use of the MP2 CV correction, while quite reasonable, will still give errors greater than our desired accuracy. The scalar relativistic (SR) corrections are about 25% of the CV correction, but they cannot be ignored for a desired accuracy of ±1 kcal/mol. The error in calculating the SR corrections at the MP2 level compared to the CCSD(T) level is much smaller than calculating the CV corrections with a largest difference of ∼0.3 kcal/mol for C_8H_{18}. The $\Delta E_{\mathrm{SR-DK}}$(MP2) corrections are −1.95, −1.46, and −1.22 kcal/mol for C_8H_{18}, C_6H_{14}, and C_5H_{12}, respectively.

We first compare our results for C_4H_{10} with those we have published previously[14] based on essentially the same procedure, but with a different geometry optimization and a different method of calculation for the energy of the C atom. Previously, we calculated the energy of the C atom at the unrestricted CCSD(T) (UCCSD(T)) or restricted CCSD(T) (RCCSD(T)) levels. ΔE_{SR} was calculated in the previous work as the sum of the mass−velocity and one-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian[45] obtained at the CISD/VTZ level. Core/valence calculations were done at the same level as used here except for the differences in how the atomic energy of C was calculated. Our previous atomization energies for butane are 1219.0 and 1220.0 kcal/mol with the C atom energies calculated at the UCCSD(T) and RCCSD(T) levels, respectively; our current value lies right in the middle of these two values at 1219.4 kcal/mol. All of the values are in excellent agreement with the experimental value of 1219.4 ± 0.6 kcal/mol.

The calculated heats of formation for octane, hexane, and pentane at both 0 and 298 K are given and compared to experiment in Table 4. The 298 K theoretical values are in excellent agreement with experiment, differing at most by 0.30 kcal/mol for octane, which is within our desired uncertainty of ±1 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 ΔH_f(C) is 0.8 kcal/mol. Our value of −50.20 kcal/mol for $\Delta H_f^{298}(C_8H_{18})$, octane's heat of formation, compares favorably to the G3 value of −50.74 kcal/mol.[2] 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 C_8H_{18} is −2.3 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-C_4H_{10} and n-C_5H_{12}, 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:

$$C_4H_{10} + C_5H_{12} \rightarrow C_8H_{18} + CH_4 \tag{2}$$

$$C_4H_{10} + C_6H_{14} \rightarrow C_8H_{18} + C_2H_6 \tag{3}$$

TABLE 5: Isodesmic Reaction Energies in kcal/mol[a]

approach	reaction 2		reaction 3	
		$\Delta H_f^0(C_8H_{18})^b$		$\Delta H_f^0(C_8H_{18})^b$
experiment (ref 1)	−3.9 ± 0.7	−38.70	−0.7 ± 0.7	−38.70
MP2/aVDZ	−4.2	−39.0	−0.5	−38.5
MP2/aVTZ	−3.5	−38.3	−1.1	−39.1
MP2/aVQZ	−3.5	−38.3	−0.2	−38.2
MP2/CBS	−3.7	−38.5	0.3	−37.8
CCSD(T)/aVDZ	−4.2	−39.0	−0.9	−38.9
CCSD(T)/aVTZ	−3.3	−38.1	−0.4	−38.4
CCSD(T)/aVQZ	−3.3	−38.1	−0.4	−38.4
CCSD(T)/CBS	−3.3	−38.1	−0.3	−38.3
CCSD(T)/CBS + all corrections[c]	−3.2	−38.0	−0.2	−38.2

[a] ΔZPE(reaction 2) = −1.0 kcal/mol. ΔZPE(reaction 3) = −0.2 kcal/mol. [b] Heat of formation of C_8H_{18} at 0 K calculated from the experimental heats of formation of the alkanes given in reactions 2 and 3 and the electronic reaction energies except for the experimental heat of formation of C_8H_{18} given in the first line. [c] See Table 3 for a definition of correction quantities.

We present the results of calculations at different levels for the isodesmic reactions in Table 5. The isodesmic energies reported in Table 5 are for the reactions at 0 K, and only the valence electronic and zero point contributions are given unless noted. The ΔZPE corrections are −1.0 kcal/mol for reaction 2 and −0.2 kcal/mol for reaction 3. The overall agreement is good within 1 kcal/mol for all methods and basis sets. The resulting heats of formation of C_8H_{18} are also given in Table 5 based on the calculated reaction energies and the 0 K experimental heats of formation of the remaining alkanes in the reaction. An error bar of ±0.43 kcal/mol is expected for the heat of formation of C_8H_{18} based on reaction 2 from the experimental error bars, and for reaction 3, an error bar of ±0.40 kcal/mol is expected. The contributions for the terms other than the electronic energy and zero point energy effects are small, suggesting that the ΔE_{CV} and ΔE_{SR} contributions are approximately additive in terms of the number of CH_2 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 C_5H_{12}, C_6H_{14}, and C_8H_{18} 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.

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