Heat of Formation of Singlet Methylene

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Abstract: The heat of formation, $\Delta H_f°_0$, of CH_2 ($^1A_1$) has been determined by ab initio calculations including extrapolation to the complete basis set (CBS) limit. The calculated value for the heat of formation is $\Delta H_f°_0 = 102.0 \pm 0.7$ kcal/mol, which agrees with both the experimental upper limit of 102.6 kcal/mol and the average of several direct experimental measurements, 101.8 ± 0.5 kcal/mol. The contribution of the 1s, valence correlation energy is +2.04 kcal/mol.

The heat of formation of singlet methylene is of considerable interest for studies of chemical reactions such as the rearrangement of propene to cyclopropane.[1] We have determined this heat of formation using ab initio calculations including extrapolation to the complete basis set (CBS) limit.[2] The calculated value, 102.0 ± 0.7 kcal/mol, lies within the uncertainty in the experimental value, 101.8 ± 0.5 kcal/mol.

Method and Results

To find the heat of formation, $\Delta H_f°_0$, of CH_2 ($^1A_1$), we have studied to gas-phase reaction:

$$H_2 + CH_2\ (^1A_1) \rightarrow CH_4$$

The standard heats of formation at 0 K of H_2 and CH_4 are known by definition and experiment[3d] to be 0.0 and −15.97 ± 0.1 kcal/mol, respectively.

We used the experimental geometry for the separate species in calculating the total energy. The internuclear distance for the hydrogen molecule[3b] is 0.7414 Å. The internuclear distance and H–C–H angle for CH_2 ($^1A_1$) are 1.110 Å and 102.4°, respectively,[3b] and for methane[3b] the internuclear distance is 1.085 Å and the H–C–H angles are 109.47°.

The calculated total energy change for the reaction must be corrected for the zero-point energy change including anharmonicity differences to find $\Delta H_f°_0$. The harmonic zero-point energy can be calculated with the experimental fundamental frequencies. The vibrational frequency of hydrogen[3b] is 4160.2 cm^{-1}. The symmetric and antisymmetric vibrational frequencies for singlet methylene are 2805.9 and 2864.5 cm^{-1}, respectively,[3e] and the bending frequency[3c] is 1352.6 cm^{-1}. Methane[3a] has a singlet at 2917 cm^{-1}, a doublet at 1534 cm^{-1}, and two triplets at 1306 and 3019 cm^{-1}. The anharmonicity corrections to the zero-point energies for the hydrogen molecule,[3b] methylene,[3f] and methane[3a] are 117.91, 397, and 903.7 cm^{-1}, respectively. Because of the lack of enough information about the anharmonicity correction for singlet methylene, we used the value for triplet methylene as an approximation. The anharmonicity correction for the bending mode in triplet methylene (117.91 cm^{-1} or 0.33 kcal/mol) is undoubtedly too large for singlet methylene, but the error from using this value to obtain $\Delta H_f°_0$ is clearly less than 0.3 kcal/mol. We believe the error in the zero-point energy correction is closer to ±0.1 kcal/mol.

The total energy change for a chemical reaction can be expanded in a Møller–Plesset perturbation expansion.[4] A reliable calculation of the energy change requires that *each* order of perturbation theory be converged with respect to expansion of the basis set *and* that enough terms have been included in the perturbation series to achieve a converged result.

In Table I we present the self-consistent field (SCF) contribution to the heat of formation calculated with basis sets ranging from the simple STO-3G to the large quadruple-ζ plus triple polarization plus 2f (QZ+TP+2f) atomic pair natural orbital (APNO) basis set.[2d,2f] As the basis set is improved, the SCF contribution to the heat of formation converges monotonically from above. Extrapolation of these calculations on the basis of the l^{-6} convergence of higher angular momentum (i.e. g, h, etc.) contributions gives the complete basis set (CBS) SCF limit.[2d,2f] The small changes from the QZ+TP result to the QZ+TP+2f result and from the QZ+TP+2f result to the CBS extrapolation suggest that the CBS SCF contribution to the reaction energy is converged to within ±0.1 kcal/mol.

Table II examines the convergence of the correlation energy contribution to the heat of formation. First we examine the frozen core (FC) approximation in which we include only the correlation energy of the valence electrons. The first set of calculations in Table II shows that, as the basis set is improved, the direct Møller–Plesset second-order (MP2) contribution converges to the complete basis limit from below. Since larger basis sets recover more of the correlation energy, they favor CH_4, which has more electron pair interactions. Extrapolation[2d-2f] to the complete basis set (CBS2) limit using the N^{-1} asymptotic convergence[2a-2c] of N-configuration pair natural orbital expansions[5] convergers from above. Evidently, the low-lying natural orbitals of CH_2 are not as well described by APNOs and require more flexibility in the basis set. Correction for the basis set superposition error (BSSE) brings the two approaches into good agreement ($\Delta H_f°_0$ from MP2(FC) = +17.46 ± 0.24 kcal/mol).

The third-order contribution, MP3(FC), is much smaller and converges rapidly with expansion of the basis set to −4.60 ± 0.05 kcal/mol. The fourth-order contribution, MP4(FC), is still smaller but converges less rapidly with the expansion of the basis set to −0.17 ± 0.3 kcal/mol.

The above error estimates presume that adding g, h, i, etc., basis functions will have a smaller effect than the addition of f functions. The N^{-1} convergence of the expansion in N natural orbitals requires that this is true for each individual molecule but not necessarily for the small differences between molecular energies. However, we believe that this is a reasonable assumption.

At first glance, the expansion in orders of MP perturbation theory appears to be sufficiently converged at fourth order that higher orders will contribute less to $\Delta H_f°_0$ than the basis set truncation error in the second- and fourth-order contributions. Unfortunately, a more careful consideration of the convergence

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Table I. Convergence of the SCF Energy (hartree) for the Reaction $H_2 + CH_2\ (^1A_1) \rightarrow CH_4$ and the Resulting $\Delta H_f{}^\circ{}_0\ CH_2\ (^1A_1)$ (kcal/mol)

basis set	H_2	CH_2	CH_4	reaction	$\Delta H_f{}^\circ{}_0\ CH_2\ (^1A_1)$
STO-3G	-1.116 68	-38.371 98	-39.726 85	-0.238 19	+121.23
4-31G	-1.126 73	-38.810 05	-40.139 72	-0.202 95	+99.11
6-31G	-1.126 73	-38.853 05	-40.180 53	-0.200 75	+97.73
6-31G**	-1.131 28	-38.876 16	-40.201 70	-0.194 26	+93.66
DZ+P; APNO[a]	-1.130 28	-38.886 23	-40.207 04	-0.190 53	+91.33
TZ+DP; APNO[b]	-1.131 67	-38.893 71	-40.213 27	-0.187 89	+89.66
QZ+TP; APNO	-1.133 38	-38.894 93	-40.215 73	-0.187 42	+89.37
QZ+TP+2f; APNO	-1.133 38	-38.895 18	-40.216 09	-0.187 53	+89.44
l^{-6} extrapolation	-0.000 08	-0.000 15	-0.000 30	-0.000 07	+0.04
CBS SCF	-1.133 46	-38.895 33	-40.216 39	-0.187 60	+89.48

[a] This is the same as the {LL} basis set in Table II. [b] This is the same as the {KK, KL, LL, LL′} basis set in Table II.

Table II. Convergence of the Correlation Energy (hartree) for the Reaction $H_2 + CH_2\ (^1A_1) \rightarrow CH_4$ and the Resulting $\Delta H_f{}^\circ{}_0\ CH_2\ (^1A_1)$ (kcal/mol)

method and basis set	H_2	CH_2	CH_4	reaction	$\Delta H_f{}^\circ{}_0\ CH_2\ (^1A_1)$
MP2(FC)					
6-31G**	-0.026 34	-0.110 98	-0.162 93	-0.025 60	+16.06
DZ+P; APNO[a]	-0.028 01	-0.115 67	-0.169 73	-0.026 05	+16.35
TZ+DP	-0.029 32	-0.124 02	-0.178 47	-0.025 13	+15.77
QZ+TP	-0.030 40	-0.130 24	-0.187 70	-0.027 06	+16.98
QZ+TP+2f	-0.030 40	-0.140 51	-0.198 35	-0.027 44	+17.22
CBS2(FC)					
DZ+P; APNO[a]	-0.034 22	-0.149 12	-0.216 05	-0.032 71	+20.52
TZ+DP	-0.034 54	-0.153 87	-0.219 59	-0.031 18	+19.57
QZ+TP	-0.034 69	-0.156 01	-0.220 18	-0.029 48	+18.50
QZ+TP+BSSE[b]	-0.034 76	-0.157 27	-0.220 18	-0.028 16	+17.67
MP3(FC)					
6-31G**	-0.005 52	-0.019 12	-0.018 22	+0.006 42	-4.03
DZ+P; APNO[a]	-0.006 48	-0.020 32	-0.019 09	+0.007 72	-4.84
TZ+DP	-0.006 31	-0.020 78	-0.019 67	+0.007 42	-4.66
QZ+TP	-0.005 93	-0.019 78	-0.018 44	+0.007 27	-4.56
QZ+TP+2f	-0.005 93	-0.019 56	-0.018 16	+0.007 33	-4.60
MP4(FC)					
6-31G**	-0.001 42	-0.005 68	-0.005 79	+0.001 31	-0.82
DZ+P; APNO[a]	-0.001 59	-0.005 96	-0.006 44	+0.001 11	-0.70
TZ+DP	-0.001 56	-0.006 52	-0.007 12	+0.000 96	-0.60
QZ+TP	-0.001 54	-0.006 74	-0.007 64	+0.000 64	-0.40
QZ+TP+2f	-0.001 54	-0.006 86	-0.008 13	+0.000 27	-0.17
MP4(FC)/total					
6-31G**	-0.033 28	-0.135 78	-0.186 94	-0.017 88	+11.22
DZ+P; APNO[a]	-0.036 08	-0.141 96	-0.195 25	-0.017 22	+10.81
TZ+DP	-0.037 19	-0.151 32	-0.205 26	-0.016 75	+10.51
QZ+TP	-0.037 87	-0.156 76	-0.213 78	-0.019 15	+12.02
QZ+TP+2f	-0.037 87	-0.166 93	-0.224 64	-0.019 84	+12.45

[a] This frozen-core DZ+P size basis set is obtained from the {KK, KL, LL} full DZ+P basis set in ref 2f by deleting the 2s′ and 2p′ functions, which correlate the (1s, 1s) pair, and the 4p″ and 4d″ functions, which correlate the (1s, 2p) pairs. [b] This calculation included the correction for the basis set superposition error (BSSE) on both H2 and CH2.

suggests that this is not true. The ($3a_1$, $1b_1$) near degeneracy in CH_2 makes the perturbation expansion relatively slowly convergent. As a result, the MP3 contribution is larger for CH_2 than for CH_4 (Table II). However, the larger number of three-body interactions in CH_4 makes the MP4(FC) triple-excitation contribution (-0.005 69 hartree) much larger than that for CH_2 (-0.002 99 hartree). The remaining MP4(FC) contributions from single, double, and quadruple excitations are larger in CH_2 (-0.003 87) than in CH_4 (-0.002 44), indicating that the near-degeneracy effect in CH_2 will dominate again beyond fourth order so that the full CI $\Delta H_f{}^\circ{}_0$ should be less than the MP4 limit.

We have shown previously[2d,2f] that including pair energies[6] to infinite order and pair coupling terms[7] to third order gives a $CBS^{(\infty,3)}$ correlation energy that is very close to a full CI. It is appropriate to test this approximation in the present application to determine the accuracy when dealing with the ($3a_1$, $1b_1$) near degeneracy in CH_2. The full CI correlation energy of CH_2 ($^1A_1$) with a Dunning DZ+P basis set[8] has been determined by Bauschlicher and Taylor.[9] We have determined the MP2, MP3, MP4, and pair CI energies with the same basis set at the same geometry. The difference between the full CI energy and the MP2 energy is -0.031 06 hartree. The sum of the MP3 and MP4 contributions is only -0.026 07 hartree, confirming a relatively large contribution of -0.004 99 hartree from fifth and higher orders of Møller–Plesset perturbation theory. The sum of the pair CI energies and the third-order pair coupling terms, $MP^{(\infty,3)}$, gives -0.034 99 hartree for the contribution beyond second order, indicating a contribution of +0.003 93 hartree from fourth and higher order pair coupling terms. The $MP^{(\infty,3)}$ approximation is comparable in accuracy to the MP4 approximation for CH_2 ($^1A_1$). However, extrapolation to the complete basis set limit reduces the discrepancy between the $MP^{(\infty,3)}$ energy and the full CI energy. The difference between the $CBS^{(\infty,3)}$ and the CBS2 energies (-0.029 07 hartree) is considerably closer to the full CI contribution beyond second order (-0.031 06 hartree).

In a recent paper[2f] we introduced a $CBS^{(\infty,3)}$/{KK, KL, LL, LL′} APNO model chemistry employing DZ+P sets of APNOs for the (1s, 1s), (1s, valence), and (valence, valence) intraorbital and (valence, valence) interorbital pairs. Using this model, we obtain a correlation energy contribution to the $\Delta H_f{}^\circ{}_0$ for CH_2 ($^1A_1$) of

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Table III. Convergence of the CBS Correlation Energy (hartree) for the Reaction $H_2 + CH_2\ (^1A_1) \rightarrow CH_4$ and the Resulting $\Delta H_{\mathrm{f}}{}^{\circ}{}_0\ CH_2\ (^1A_1)$ (kcal/mol)

method and basis set	H_2	CH_2	CH_4	reaction	$\Delta H_{\mathrm{f}}{}^{\circ}{}_0\ CH_2\ (^1A_1)$
CBS2(FC)					
DZ+P = {LL}; APNO[a]	−0.034 22	−0.149 12	−0.216 05	−0.032 71	+20.52
{KK, KL, LL}	−0.034 22	−0.152 64	−0.217 96	−0.031 10	+19.52
TZ+DP = {LL, LL′}	−0.034 54	−0.153 87	−0.219 59	−0.031 18	+19.57
{KK, KL, LL, LL′}	−0.034 54	−0.155 47	−0.219 93	−0.029 92	+18.78
QZ+TP+BSSE[b]	0.034 76	−0.157 27	−0.220 18	−0.028 16	+17.67
CBS$^{(\infty,3)}$(FC)					
DZ+P = {LL}; APNO[a]	−0.040 02	−0.170 74	−0.231 82	−0.021 06	+13.22
{KK, KL, LL}	−0.040 02	−0.174 98	−0.232 78	−0.017 79	+11.16
TZ+DP = {LL, LL′}	−0.040 53	−0.177 06	−0.235 24	−0.017 65	+11.08
{KK, KL, LL, LL′}	−0.040 53	−0.178 24	−0.235 45	−0.016 68	+10.47
CBS$^{(\infty,3)}$					
{KK, KL, LL}; APNO	−0.040 02	−0.229 07	−0.290 64	−0.021 55	+13.52
{KK, KL, LL, LL′}	−0.040 53	−0.233 17	−0.293 63	−0.019 93	+12.51

[a] This frozen-core DZ+P size basis set is obtained from the {KK, KL, LL} full DZ+P basis set in ref 2f by deleting the 2s′ and 2p′ functions, which correlate the (1s, 1s) pair, and the 4p″ and 4d″ functions, which correlate the (1s, 2p) pairs. [b] This calculation included the correction for the basis set superposition error (BSSE) on both H2 and CH2.

Table IV. Summary of the More Cost Effective Calculations of $\Delta H_{\mathrm{f}}{}^{\circ}{}_0$ (kcal/mol) for $CH_2\ (^1A_1)$

	method				
basis set	SCF	MP2(FC)	MP3(FC)	CBS$^{(\infty,3)}$(FC)	CBS$^{(\infty,3)}$
STO-3G	121.23				
6-31G**	93.66	109.72	105.69		
TZ+DP	89.66	105.43	100.77	100.74	101.99[a]
QZ+TP+2f	89.44	106.66	102.06		
est limit	89.48	106.94	102.34	100.24	101.6 ± 0.5

[a] This calculation included the KK and KL basis functions for the inner shell.

+12.51 kcal/mol, in good agreement with the MP4(FC)/QZ+TP+2f results +12.45 kcal/mol and an estimated MP4(FC) limit of +12.69 kcal/mol. Unfortunately, the very close agreement is fortuitous.

Detailed results obtained with our model chemistry are presented in Table III along with results obtained with the same method with several other basis sets for comparison. If we choose the DZ+P {LL} basis set as a starting point, then the addition of KL basis functions (optimized for atomic 1s, valence pairs) or LL′ basis functions (optimized for atomic valence–valence interorbital pairs) or correction for the BSSE will reduce the CBS2(FC) value for $\Delta H_{\mathrm{f}}{}^{\circ}{}_0$ by about 1 kcal/mol. These basis set effects are roughly additive. Correction for BSSE cannot be part of a model chemistry, since the energy of a molecule becomes dependent on the reaction under study. However, the CBS2(FC)/QZ+TP+BSSE result is useful to demonstrate the lack of basis set saturation for CH_2 in our CBS/{KK, KL, LL, LL′} model chemistry. Evidence that this lack of saturation persists in higher order calculations comes from comparison of our CBS$^{(\infty,3)}$(FC)/{KK, KL, LL, LL′} correlation energy for CH_2 (−0.178 24 hartree) with the CASSCF-SOCI+Q/[5s4p3d2f1g,4s3p2d] result (−0.179 49 hartree) of Bauschlicher, Langhoff, and Taylor.[10] Our CBS model chemistry clearly underestimates the valence-shell correlation energy of CH_2. Nevertheless, it is a significant improvement over the direct MP4(FC) result with the same [4s4p3d,3s2p] basis set (−0.152 50 hartree).

The effect of the lack of basis set saturation on the CBS$^{(\infty,3)}$/{KK, KL, LL, LL′} energy for CH_2 is probably to overestimate $\Delta H_{\mathrm{f}}{}^{\circ}{}_0$ by about 0.5 kcal/mol.

Calculations at the CBS$^{(\infty,3)}$ level with and without the FC approximation indicate that the contribution of the inner shell–valence interactions to the heat of formation of CH_2 is +2.04 kcal/mol (Table III). Direct MP2 calculations give an inner shell–valence contribution of +0.74 kcal/mol with the {KK, KL, LL} basis set and +1.09 kcal/mol with the {KK, KL, LL, LL′} basis set.

The CBS program uses GAUSSIAN82[11] to evaluate all necessary integrals and determine the SCF energy and then performs the CBS extrapolation of the correlation energy. All calculations employing [spd,sp] basis sets were performed on a DEC Micro Vax-II computer. The MP4(FC)/QZ+TP+2f calculations were performed on the Cray X-MP supercomputer at the Pittsburgh Supercomputer Center, which was available through the NSF Office of Advanced Scientific Computing.

Conclusions

The total calculated complete basis set value for the heat of formation of singlet methylene is obtained by adding the CBS SCF contribution (Table I) to the CBS$^{(\infty,3)}$/{KK, KL, LL, LL′} APNO correlation contribution (Table III). Our CBS result for the heat of formation of methylene is 101.99 kcal/mol. The MP4(FC)/QZ+TP+2f calculation gives 101.89 kcal/mol, and the CBS SCF energy plus the estimated MP4(FC) limit gives 102.17 kcal/mol. Unfortunately, the agreement with the CBS result comes from the cancellation of a contribution from terms beyond fourth order (−2 kcal/mol), by a contribution from 1s, valence interactions (+2 kcal/mol). Using our error estimates above, we conclude that $\Delta H_{\mathrm{f}}{}^{\circ}{}_0 = +102.0 \pm 0.7$ kcal/mol, which is in agreement with both the average of several direct experimental values[12] (101.8 ± 0.5 kcal/mol) and the experimental upper limit[13] (102.6 kcal/mol).

The final results for $\Delta H_{\mathrm{f}}{}^{\circ}{}_0$ obtained with the most cost effective calculations are summarized in Table IV. The SCF and MP2 contributions to $\Delta H_{\mathrm{f}}{}^{\circ}{}_0$ are large and must be converged with expansion of the basis set. The MP3 contribution is also significant but converges rapidly with basis set expansion. The core contribution is small and cancels contributions from higher orders of perturbation theory. The minimum requirements for a reliable calculation are reasonable estimation of the CBS limits for ΔE(SCF) and $\Delta E^{(2)}$(FC) and inclusion of $\Delta E^{(3)}$(FC).

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Registry No. H_2, 1333-74-0; CH_4, 74-82-8; CH_2, 2465-56-7.

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