

Heats of formation of CCl and CCl₂ from *ab initio* quantum chemistry

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(Received 16 July 2001; accepted 20 July 2001)

High level *ab initio* electronic structure theory has been used to calculate the heats of formation of CCl and CCl₂. The calculations were done at the CCSD(T) level with new correlation-consistent basis sets up through augmented hexuple- ζ including tight *d* functions on the Cl and then extrapolated to the complete basis set limit. Additional corrections for core/valence correlation, relativistic effects both scalar and atomic spin-orbit, and zero-point energies have been included. The heat of formation at 0 K of CCl is 103.1 ± 0.4 kcal/mol and that of CCl₂ is 55.1 ± 0.4 kcal/mol.

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We have been developing a composite theoretical approach to reliably predict molecular heats of formation without recourse to empirical parameters.¹⁻⁹ Our approach starts with existing, reliable thermodynamic values obtained from either experiment or theory. We use experimental atomic heats of formation, which are difficult to obtain theoretically, as well as molecular and atomic spin-orbit splittings (if available). High-level *ab initio* electronic structure methods are then used to calculate the molecular atomization energy. The energy of the valence electrons are calculated by using coupled cluster methods including single, double, and connected triple excitations [CCSD(T)], with the latter being handled perturbatively.¹⁰⁻¹² The CCSD(T) energies are extrapolated to the complete basis set (CBS) limit using the correlation consistent basis sets (cc-pVnZ) from Dunning and co-workers.¹³⁻¹⁵ This family of basis sets is chosen because of the regularity with which it approaches the CBS limit. In addition, core-valence (ΔE_{CV}) and relativistic, both spin-orbit and scalar relativistic, corrections to the dissociation energy are required for <1 kcal/mol accuracy. Finally, one needs an accurate zero-point energy in order to calculate the total atomization energy at 0 K, ΣD_0 , and hence ΔH_f at 0 K given the atomic heats of formation.

The heat of formation of CCl₂ is of interest as it is a prototypical halogenated carbene and is important in the decomposition processes of chlorinated hydrocarbons. We recently reported $\Delta H_f(\text{CCl})$ and $\Delta H_f(\text{CCl}_2)$ at 0 K based on a quantum chemical approach using total dissociation energies calculated by extrapolating CCSD(T) results to the CBS limit.¹⁶ In this calculation, we used the cc-pVnZ basis sets with $n_{\text{max}}=5$ for CCl and $n_{\text{max}}=Q(4)$ for CCl₂. We included core-valence corrections but did not include any effects of relativity including the spin-orbit correction to the atoms which decreases the dissociation energy of CCl₂ by 1.76 kcal/mol. Another recent paper reported a similar study using the same approach with the aug-cc-pVnZ basis sets and $n_{\text{max}}=4$.¹⁷ These authors did include relativistic corrections

(both scalar and spin-orbit). They obtained $\Delta H_f(\text{CCl}_2) = 54.7 \pm 1$ kcal/mol as compared to our previous value of 53.0 kcal/mol. The latter value would change to 54.8 kcal/mol if we include the spin-orbit correction for the atoms. In addition, we have been exploring the role of tight *d* functions in calculating atomization energies of species containing second row elements and have found that such functions are necessary to obtain accurate dissociation energies.¹⁸ Thus, we have recalculated $\Delta H_f(\text{CCl})$ and $\Delta H_f(\text{CCl}_2)$ using new tight *d* augmented basis sets up to $n_{\text{max}}=6$.

For the present study, we used the new diffuse function augmented correlation consistent basis sets with tight *d* functions, aug-cc-pV(*n*+*d*)Z, for Cl and the standard aug-cc-pVnZ sets for C ($n=D$ through 6). Only the spherical components (5-*d*, 7-*f*, 9-*g*, 11-*h*, and 13-*i*) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.¹⁹ The open-shell CCSD(T) calculations were carried out at the R/UCCSD(T) level, where a restricted open-shell Hartree-Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.²⁰⁻²² The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

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

where $n=2$ (DZ), 3 (TZ), etc., as first proposed by Peterson *et al.*²³ In addition, extrapolations of the CCSD(T) correlation energies were also performed with the two-parameter function^{24,25}

$$E(n) = E_{\text{CBS}} + A l_{\text{max}}^{-3}, \quad (2)$$

where l_{max} is the highest *l* value in the basis set and is equal to n . The CBS limit total energy was obtained via Eq. (2) by combining the extrapolated correlation energy with the aug-cc-pV(6+*d*) Hartree-Fock energy. The spread between

TABLE I. Contributions to the total energy for C, Cl, CCl, and CCl₂.

Contribution ^a	C	Cl	CCl	CCl ₂
aug-cc-pV(6+d)Z	-37.788 755	-459.703 832	-497.647 016	-957.476 207
Est. CBS ^b	-37.789 371	-459.707 159	-497.651 588	-957.484 514
E_{CV} ^c	-0.052 214	-0.323 644	-0.376 449	-0.700 402
E_{SR} ^d	-0.014 986	-1.403 868	-1.418 557	-2.822 182
ΔE_{elec}			97.30±0.18	176.22±0.16
ΔE_{CV}			0.37	0.56
ΔE_{SR}			-0.19±0.1	-0.34±0.1
ΔE_{SO} ^e			-0.73	-1.76
ΔE_{ZPE} ^f			-1.25	-2.58±0.04
ΣD_0 ^g			95.50±0.3	172.10±0.3
$\Delta H_f(0\text{ K})$			103.1±0.4	55.1±0.4

^aTotal energies in hartrees and energy differences in kcal/mol. The final estimated uncertainties in ΣD_0 and ΔH_f do not include the intrinsic errors of the CCSD(T) method.

^bEstimated frozen core, CCSD(T) complete basis set energies obtained from Eq. (2) using aug-cc-pV(5+d)Z and aug-cc-pV(6+d)Z correlation energies and the aug-cc-pV(6+d)Z Hartree-Fock energy. Use of Eq. (1) with the aDZ-aQZ basis sets yields ΔE_{elec} values of 97.12 kcal/mol for CCl and 176.06 kcal/mol for CCl₂.

^cCore/valence corrections were obtained from R/UCSD(T)/cc-pwCVQZ calculations.

^dScalar relativistic corrections were obtained from CISD(FC)/unc-aug-cc-pV(Q+d)Z calculations.

^eNet spin-orbit correction to the atomization energy.

^fContributions from the zero-point vibrational energies of CCl and CCl₂. See the text.

^g $\Sigma D_0 = \Delta E_{elec} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} + \Delta E_{ZPE}$.

the CBS values obtained via Eqs. (1) and (2) were used to estimate the uncertainty in the extrapolations.

The geometries were optimized at the frozen core CCSD(T)/aug-cc-pV(Q+d)Z level of theory giving $r(\text{CCl})=1.6520\text{ \AA}$ for the ²Π ground state of CCl (experimental value²⁶ is 1.6452 Å) and $r(\text{CCl})=1.7175\text{ \AA}$ and $\langle \text{ClCCl} \rangle = 109.20^\circ$ for the ¹A₁ ground state of CCl₂ as compared to the microwave r_0 values²⁷ of 1.7157 and 109.2° for CCl₂. The zero-point energy of CCl is derived from the accurate spectroscopic constants of Jin *et al.*,²⁸ $\omega_e = 876.90\text{ cm}^{-1}$ and $\omega_e x_e = 5.45\text{ cm}^{-1}$. These can be compared to the quantities calculated from a sixth-order polynomial fit to seven near-equilibrium energies at the CCSD(T)/aug-cc-pV(5+d)Z level of theory, $\omega_e = 877.5\text{ cm}^{-1}$ and $\omega_e x_e = 5.3\text{ cm}^{-1}$. The molecular zero-point energy for CCl₂ was derived from the experimental band origins.²⁹ The experimental values are 730 and 335 cm⁻¹ for the symmetric stretch and bend, respectively, in the gas phase and an asymmetric stretching frequency of 748 cm⁻¹ from an argon matrix study. These can be compared to CCSD(T)/cc-pVQZ harmonic values for the symmetric modes of 731 and 340 cm⁻¹ obtained in this work. For the asymmetric stretch, we also note the CCSD(T)/cc-pVTZ harmonic value of 760 cm⁻¹ from Ref. 17. The CCSD(T) values can be used to provide an estimate of the error in the CCl₂ zero-point energy of ±0.04 kcal/mol.

ΔE_{CV} was obtained at the CCSD(T)/cc-pwCVQZ level of theory from both valence-only correlated calculations and those where correlation of the C 1s and Cl 2s2p electrons were also included. It should be noted that it is generally not reliable to derive ΔE_{CV} using two different basis sets, e.g., CCSD(T)/cc-pVQZ for the valence-only calculation and CCSD(T)/cc-pwCVQZ for the all-electron case, since the core-valence correlating functions can have nonnegligible effects in valence-only calculations and their neglect can lead to an overestimate of ΔE_{CV} . As in most electronic structure

calculations, the present work does not explicitly account for any zero-field spin-orbit splittings, but instead yields a weighted average of the available multiplets. In order to correct for this effect, we apply an atomic spin-orbit correction of -0.08 kcal/mol for C and -0.84 kcal/mol for Cl based on the excitation energies of Moore.³⁰ For CCl, a molecular spin-orbit correction of 0.19 kcal/mol is available from experiment.²⁸ 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 included at the CISD level of theory using an uncontracted aug-cc-pV(Q+d)Z basis set in the frozen core approximation. ΔE_{SR} is taken as the sum of the mass-velocity and one-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian,³¹ and we assign an estimated uncertainty of ±0.1 kcal/mol to this quantity.

The various components of the energy are shown in Table I. The error bars for the valence electronic atomization energies are estimated as the difference between the results of Eq. (1) using the DZ through QZ basis sets and Eq. (2) using the 5Z and 6Z sets, which yields error limits of ±0.18 kcal/mol for CCl and ±0.16 kcal/mol for CCl₂. By combining our computed ΣD_0 values with the known³² heats of formation at 0 K for the elements ($\Delta H_f^0(\text{C})=169.98\pm 0.1$ kcal/mol and $\Delta H_f^0(\text{Cl})=28.590\pm 0.001$ kcal/mol), we derive ΔH_f^0 values for CCl and CCl₂ as shown in Table I. The heat of formation of CCl at 0 K is 103.1±0.4 kcal/mol as compared to our previous value of 102.5 kcal/mol. Most of the difference is due to our previous neglect of relativistic effects which account for 0.92 kcal/mol. Our current value is in reasonable agreement with the recent experimental determination by Jesinger and Squires³³ of 105.0±3.1 kcal/mol (105.9±3.1 kcal/mol at 298 K). For $\Delta H_f(\text{CCl}_2)$, our latest, best prediction is 55.1±0.4 kcal/mol as compared to our previous value of 53.0 kcal/mol. Again, most of the difference is

due to relativistic effects, which total 2.1 kcal/mol. Our result for $\Delta H_f(\text{CCl}_2)$ is larger in magnitude than the value of 54.5 ± 1 kcal/mol reported by Sendt and Bacskay.¹⁷ The difference in the two values is mostly due to the overestimation of core–valence correlation effects in Ref. 17, 1.37 versus 0.56 kcal/mol, as well as smaller contributions due to the lack of tight *d* functions in the basis sets used in their extrapolations, as well as a slightly smaller scalar relativistic correction. The G3 value for $\Delta H_f(\text{CCl}_2)$ of 54.0 kcal/mol is in qualitative agreement with our final predicted value. The heat of formation of CCl₂ was measured by Paulino and Squires³⁴ as 52.1 ± 3.4 kcal/mol at 298 K (51.8 ± 3.4 kcal/mol at 0 K). The Squires group³⁵ later revised this value upwards to 55.0 ± 2.0 kcal/mol at 298 K (54.7 ± 2.0 kcal/mol at 0 K). The revised value is in excellent agreement with our latest calculated value.

This research was performed in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL). Operation of the EMSL is funded by the Office of Biological and Environmental Research in the U.S. Department of Energy (DOE). PNNL is operated by Battelle for the U.S. DOE under Contract No. DE-AC06-76RLO 1830. K.A.P. was supported by the Division of Chemical Sciences in the Office of Basis Energy Sciences of the U.S. DOE.

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