High-Accuracy Extrapolated Ab Initio Thermochemistry of Vinyl Chloride

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Applying a modified "high accuracy extrapolated ab initio thermochemistry" (HEAT) scheme, the standard heat of formation of vinyl chloride at 0 K is computed to be 29.79 ± 1 kJ/mol and at 298.15 K to be 20.9 ± 2 kJ/mol, thus resolving earlier discrepancies among the available experimental values, which span a range from 21 up to 38 kJ/mol. The enthalpies of the reactions $C_2H_4 + Cl_2 \rightarrow CH_2CHCl + HCl$ and $C_2H_2 + HCl \rightarrow CH_2CHCl$ at 298.15 K are determined to be −123.0 and −113.9 ± 2 kJ/mol, respectively.

1. Introduction

Significant progress has been recently achieved in the field of theoretical high-accuracy thermochemistry.[1−6] This has become possible due to (a) methodological developments enabling the routine inclusion of higher excitations in electron-correlated quantum chemical calculations;[7] (b) extrapolation techniques for estimating the basis set limit[8,9] in quantum chemical calculations; (c) the possibility to routinely determine anharmonic force fields using second-order vibrational perturbation theory (see, for example, refs 10−14); and (d) the availability of reliable experimental data, obtained within the active thermochemical tables (ATcT) of Ruscic and coworkers,[15] for the calibration of the theoretical schemes.

In this way, protocols such as HEAT,[4,5] W3,[2] and W4,[3] as well as focal point analysis,[6] have been developed and are capable of providing thermochemical energies (i.e., atomization energies or heats of formation) with an accuracy of 1 kJ/mol or even better.

A recent benchmark study of reaction energies using local coupled-cluster techniques revealed several discrepancies between the computed results and the available experimental data.[16,17] The problematic reactions involve vinyl chloride (CH_2CHCl) and isocyanic acid (HNCO). The discrepancies were on the order of 25 kJ/mol[16] and, thus, larger than the typical error of the coupled-cluster singles and doubles (CCSD) scheme augmented by a perturbative treatment of triple excitations (CCSD(T))[18] used in the study. Whereas a thorough theoretical investigation of the thermochemistry of HNCO has been presented in ref 19, we will focus in this computational study on vinyl chloride. To be more specific, we will investigate the two reactions

$$C_2H_4 + Cl_2 \rightarrow CH_2CHCl + HCl \tag{R1}$$

and

$$C_2H_2 + HCl \rightarrow CH_2CHCl \tag{R2}$$

as well as the heat of formation of vinyl chloride.

The reported standard heats of formation at a temperature of 298.15 K for CH_2CHCl span a range from 21 to 38.1 kJ/mol.[20−28] For the first reaction, the values when computed from the available data in the literature, again for a temperature of 298.15 K, vary between −106.7 and −123.8 kJ/mol and for the second from −96.3 to −113.4 kJ/mol. The only direct measurement reports a value of −100.66 kJ/mol for the second reaction.[22]

Considering the recent achievements in theoretical high-accuracy thermochemistry,[2−5] it should be possible to provide definitive values (with a remaining uncertainty of about 1−2 kJ/mol) for these reaction energies and for the heat of formation of vinyl chloride. In the present paper, we will thus resolve the current unsatisfactory situation concerning these enthalpies by performing a corresponding computational investigation using a slightly modified HEAT protocol.[4,5]

2. Computational Considerations

According to the thermochemical HEAT[4] protocol, the total energy of a molecule can be obtained within the following additivity assumption

$$\begin{aligned} E = {} & E_{\mathrm{HF}}^{\infty} + \Delta E_{\mathrm{CCSD(T)}}^{\infty} \\ & + \Delta E_{\mathrm{CCSDT}} + \Delta E_{\mathrm{CCSDT(Q)}} \\ & + \Delta E_{\mathrm{ZPE}}^{\mathrm{harmonic}} + \Delta E_{\mathrm{ZPE}}^{\mathrm{anharmonic}} \\ & + \Delta E_{\mathrm{REL}} + \Delta E_{\mathrm{SO}} \\ & + \Delta E_{\mathrm{DBOC}} \end{aligned} \tag{1}$$

with E_{HF}^{∞} as the basis set limit value for the Hartree−Fock (HF) energy; $\Delta E_{\mathrm{CCSD(T)}}^{\infty}$, the basis set limit for the correlation energy obtained at the CCSD(T) level;[18] $\Delta E_{\mathrm{CCSDT}}$, accounting for additional correlation effects using the CC singles, doubles, and triples model (CCSDT); and $\Delta E_{\mathrm{CCSDT(Q)}}$, representing correlation contributions due to quadruple excitations. $\Delta E_{\mathrm{ZPE}}^{\mathrm{harmonic}}$ and $\Delta E_{\mathrm{ZPE}}^{\mathrm{anharmonic}}$ denote in eq 1 the harmonic and anharmonic contributions to the vibrational zero-point energy, ΔE_{REL} accounts for relativistic corrections, and ΔE_{DBOC} is the diagonal Born−Oppenheimer correction (DBOC) necessary due to the use of the Born−Oppenheimer approximation.

In the following, we will describe in detail how the various terms in eq 1 were obtained. In principle, we follow the

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HEAT345-(Q) protocol,[5] but a few modifications are necessary because the present study involves second-row elements, which so far have not been considered within the HEAT scheme.

2.1. Molecular Geometries. All calculations have been carried out with geometries optimized at the CCSD(T) level using the cc-pCVQZ set from Dunning's hierarchy of polarized core-valence correlation-consistent basis sets.[29−31] The geometries are obtained in calculations with all electrons correlated.[32]

2.2. HF and CCSD(T) Energy. The sum of E^{∞}_{HF} and $\Delta E^{\infty}_{\mathrm{CCSD(T)}}$ provides an estimate for the nonrelativistic electronic energy within the Born−Oppenheimer approximation using the CCSD(T) method for the treatment of electron correlation. Following common practice, these two energy contributions have been obtained separately using basis set extrapolation techniques[9] based on energies obtained with hierarchical series of basis sets. For the HF energy, calculations were carried out for this purpose with the augmented correlation-consistent polarized core-valence basis sets aug-cc-pCVXZ[29−31,33,34] with $X = 3$, 4, and 5. The corresponding basis set limit is then obtained with the following extrapolation formula advocated by Feller,[8]

$$E^{X}_{\mathrm{HF}} = E^{\infty}_{\mathrm{HF}} + a\,\exp(-bX) \tag{2}$$

where E^{X}_{HF} is the HF-SCF energy obtained with the aug-cc-pCVXZ basis set. The parameters a and b as well as the extrapolated HF-SCF energy E^{∞}_{HF} are determined uniquely from three energies.

For the correlation energy, a formula derived from the atomic partial-wave expansion is used for the extrapolation to the basis set limit,[9]

$$\Delta E^{X}_{\mathrm{CCSD(T)}} = \Delta E^{\infty}_{\mathrm{CCSD(T)}} + \frac{a}{X^{3}} \tag{3}$$

In eq 3, $\Delta E^{X}_{\mathrm{CCSD(T)}}$ is the CCSD(T) correlation energy obtained with the aug-cc-pCVXZ basis set. The parameter a and the estimated basis set limit $\Delta E^{\infty}_{\mathrm{CCSD(T)}}$ are determined from two calculations. In the present work, we use correlation energies from aug-cc-pCVQZ and aug-cc-pCV5Z calculations. Note that in line with the original HEAT protocol, but different from the Wn schemes, we do not divide the correlation energy in a valence and a core-correlation energy part and instead treat both contributions up to the CCSD(T) level together. For the open-shell systems, all calculations have been performed using an unrestricted Hartree−Fock (UHF) reference.

2.3. Higher-Level Correlation Effects. Despite the never-ending success story of the CCSD(T) method, it should not be forgotten that the (T) correction is based on perturbation theory arguments.[18,35] Thus, when aiming at high accuracy in cases wherein triple corrections are large, it appears necessary to investigate correlation effects beyond CCSD(T) and, for example, to ask to what extent CCSD(T) results differ from those obtained from a full treatment of triple excitations with the CCSDT model.[36−38] Unfortunately, it is usually not possible to perform the required CCSDT calculations with the same large basis sets as the CCSD(T) computations, and this is the major reason for separating the correlation energy in a CCSD(T) contribution and those due to treatments beyond CCSD(T). This separation is, in our opinion, well-justified, because all contributions beyond CCSD(T) are expected to be rather small, and the largest contribution to the correlation energy clearly is covered at the CCSD(T) level. It thus seems to be sufficient to estimate these higher-order contributions using smaller basis sets and by taking into account valence correlation only. For the difference between CCSDT and CCSD(T), we have chosen to estimate this contribution by extrapolating the corresponding energy difference,

$$\Delta E_{\mathrm{CCSDT}} = E^{\mathrm{TQ}}_{\mathrm{CCSDT}}(\mathrm{fc}) - E^{\mathrm{TQ}}_{\mathrm{CCSD(T)}}(\mathrm{fc}) \tag{4}$$

where TQ denotes that the corresponding contribution has been obtained by extrapolating the frozen-core CCSDT and CCSD(T) energies obtained with cc-pVTZ and cc-pVQZ basis sets,[29,30] and fc denotes that the calculations have been performed in the frozen-core approximation. Open-shell systems are treated again using a UHF reference function.

Recent investigations[2−5,39] have convincingly demonstrated that the CCSDT level is not sufficient for reaching the accuracy we strive for. Due to the implementation of general CC models,[7,40,41] CC calculations beyond CCSDT are nowadays routinely possible, though still very expensive. Inclusion of quadruple excitations are feasible due to the fact that even small basis set calculations (at the cc-pVDZ level, for example) provide realistic estimates of their importance. In addition, the availability of the CCSDT(Q) scheme,[42,43] in which quadruple excitations are treated in a perturbative manner, similar to that for triple excitations in CCSD(T), increases the range of application for this kind of studies. Furthermore, in ref 5, it has been shown that CCSDT(Q) even outperforms CCSDTQ in terms of accuracy of the results. In many cases, the CCSDT(Q) results are closer to the CC singles, doubles, triples, quadruples, and pentuples (CCSDTQP) than CCSDTQ results. On the basis of these findings, we estimate the higher-order correlation contributions beyond CCSDT via

$$\Delta E_{\mathrm{CCSDT(Q)}} = E^{\mathrm{cc-pVDZ}}_{\mathrm{CCSDT(Q)}}(\mathrm{fc}) - E^{\mathrm{cc-pVDZ}}_{\mathrm{CCSDT}}(\mathrm{fc}) \tag{5}$$

2.4. Zero-Point Vibrational Energies. Zero-point vibrational energy (ZPE) contributions were determined for all species by considering the harmonic and anharmonic contributions separately. The harmonic contribution is computed at the all-electron CCSD(T) level using the cc-pCVQZ basis set,[31,34]

$$\Delta E^{\mathrm{harmonic}}_{\mathrm{ZPE}} = \sum_{i} \frac{\omega_i}{2} \tag{6}$$

whereas the anharmonic contribution to the ZPE is obtained via a second-order perturbation theory treatment,[44]

$$\Delta E^{\mathrm{anharmonic}}_{\mathrm{ZPE}} = G_0 + \frac{1}{4}\sum_{i<j} x_{ij} \tag{7}$$

with the required force fields computed at the all-electron CCSD(T) level using the cc-pCVTZ basis set.[31,34] In eqs 6 and 7, the sums run over all normal modes, i, with ω_i denoting the harmonic vibrational frequencies, and x_{ij}, the anharmonicities. Expressions for the latter can be found, for example, in ref 44. To avoid resonance denominators in the x_{ij} constants, it is necessary to include the so-called G_0 contribution (see refs 5, 19, 45−47).

2.5. Diagonal Born−Oppenheimer Correction. Because recent studies[48,49] indicated that electron-correlation effects have only a modest impact on the diagonal Born−Oppenheimer correction (DBOC), we compute this correction, which accounts for errors due to the Born−Oppenheimer approximation, at the

TABLE 1: Contributions to the HEAT345(Q) Total Energies (in Atomic Units) for the Nine Species Studied in This Work

	E_{HF}	$\Delta E_{CCSD(T)}$	ΔE_{CCSDT}	$\Delta E_{CCSDT(Q)}$	$\Delta E_{ZPE}^{harmonic}$	$\Delta E_{ZPE}^{anharmonic}$	ΔE_{rel}	ΔE_{DBOC}	ΔE_{SO}	total
H	−0.500022	0.000 000	0.000 000	0.000 000	0.000 000	0.000 000	−0.000 007	0.000 272	0.000 000	−0.499 756
H_2	−1.133 661	−0.040 912	0.000 000	0.000 000	0.010 032	−0.000 102	−0.000 010	0.000 460	0.000 000	−1.164 193
C	−37.693 774	−0.151 042	−0.000 466	−0.000 021	0.000 000	0.000 000	−0.015 090	0.001 660	−0.000 135	−37.858 869
Cl	−459.489 895	−0.665 245	−0.000 767	−0.000 144	0.000 000	0.000 000	−1.404 007	0.005 940	−0.001 340	−461.555 458
HCl	−460.112 797	−0.713 899	−0.000 540	−0.000 250	0.006 850	−0.000 054	−1.403 590	0.006 143	0.000 000	−462.218 138
Cl_2	−919.010 698	−1.395 150	−0.000 836	−0.000 703	0.001 276	−0.000 003	−2.807 653	0.011 876	0.000 000	−923.201 891
C_2H_2	−76.855 711	−0.480 387	0.000 223	−0.001 018	0.026 531	−0.000 171	−0.029 756	0.003 673	0.000 000	−77.336 617
C_2H_4	−78.070 890	−0.518 008	−0.000 167	−0.000 622	0.050 966	−0.000 507	−0.029 685	0.004 224	0.000 000	−78.564 689
C_2H_3Cl	−537.013 383	−1.19 9564	−0.000 297	−0.001 083	0.042 668	−0.000 530	−1.433 286	0.009 898	0.000 000	−539.595 576

TABLE 2: Contributions to the Total Atomization Enthalpies (TAE) (in kJ/mol) for the Six Molecules Studied in This Work[a]

	E_{HF}	$\Delta E_{CCSD(T)}$	ΔE_{CCSDT}	$\Delta E_{CCSDT(Q)}$	$\Delta E_{ZPE}^{harmonic}$	$\Delta E_{ZPE}^{anharmonic}$	ΔE_{rel}	ΔE_{DBOC}	ΔE_{SO}	total	ATcT	total-ATcT
H_2	350.81	107.41	0.00	0.00	−26.34	0.27	−0.01	0.22	0.00	432.37	432.06 ± 0.00	−0.31
HCl	322.62	127.74	−0.60	0.28	−17.99	0.14	−1.11	0.18	−3.52	427.76	427.65 ± 0.00	−0.11
Cl_2	81.15	169.76	−1.83	1.09	−3.35	0.01	−0.95	0.01	−7.04	238.85	239.24 ± 0.00	0.39
C_2H_2	1229.05	468.14	−3.03	2.56	−69.66	0.45	−1.15	0.50	−0.71	1625.15	1625.98 ± 0.07	−0.17
C_2H_4	1793.89	566.91	−2.01	1.52	−133.81	1.33	−1.37	0.48	−0.71	2226.23	2225.88 ± 0.06	−0.35
C_2H_3Cl	1669.49	609.73	−3.68	2.35	−112.03	1.39	−2.42	0.47	−4.23	2161.08	2159.54 ± 2.5 [27]	−1.63

[a] ATcT values were taken from ref 3.

TABLE 3: Calculated Standard Enthalpies of Formation at Standard Conditions (in kJ/mol) in Comparison with Experimental Values

	H_2	HCl	Cl_2	acetylene	ethylene	vinyl chloride
$\Delta_f H^0$ (0 K)	−0.31	−92.11	0.39	229.07	61.05	29.79
$\Delta_f H^0$ (0 K) from experimental TAE	0.00	−92.00	0.00	229.24	61.40	31.42
experimental $\Delta_f H^0$ (0 K)[27,61]	0.00	−92.13	0.00	227.96	60.92	30.57
$\Delta_f H^{0,harmonic}$ (298.15 K)	−0.09	−92.18	0.52	228.32	52.45	22.20
$\Delta_f H^{0,anharmonic}$ (298.15 K)	−0.09	−92.18	0.51	228.42	51.18	20.91
experimental $\Delta_f H^0$ (298.15 K) (NIST)	0.00	−92.31	0.00	226.7	52.47	21−38.1
experimental $\Delta_f H^0$ (298.15 K)[27,61]	0.00	−92.31	0.00	227.4	52.4	23.00

HF-SCF level.[50] Calculations have been performed using the aug-cc-pVTZ basis[29,30,33] and a UHF ansatz for the open-shell systems.

2.6. Relativistic Effects. Scalar relativistic effects on the total energy (ΔE_{REL}) are included by computing the corresponding corrections in a perturbative manner with the mass-velocity and one-electron Darwin terms as perturbations.[51] As discussed by Davidson et al.,[52] this is a reasonable approximation as long as only molecules with light elements are considered, as is the case in the present study. Calculations have been performed at the CCSD(T) level using the aug-cc-pCVTZ basis and a UHF ansatz for the open-shell systems. The comparison with second-order Douglas−Kroll−Hess[53] (DKH) CCSD(T) calculations from ref 3 shows excellent agreement (see results).

Spin−orbit effects were included in first order perturbation theory based on experimental data[54−56] and account for the difference between the nonrelativistic weighted average of the states and the true ground state. Values of 0.35 and 3.52 kJ/mol are taken for the carbon and the chlorine atoms, respectively.

2.7. Temperature Effects. Because we aim at a comparison with experimental thermochemical energies determined at a temperature of 298.15 K, it is essential also to include in our investigation temperature contributions. For this purpose, we assume that the rotational degrees of freedom can be treated classically and that the harmonic approximation is sufficient for the treatment of the vibrational degrees of freedom. The temperature correction, ΔE_T, to the enthalpies of formation and the reaction energies is then given as

$$\Delta E_T = \Delta E_T^{trans} + \Delta E_T^{rot} + \Delta E_T^{v} \tag{8}$$

where ΔE_T^{trans} and ΔE_T^{rot} are the classical corrections of $\pm 1/2RT$ for each translational and rotational degree of freedom gained or lost in the reaction, and R is the universal gas constant. ΔE_T^{v} is the vibrational temperature term,

$$\Delta E_T^{v} = RT \sum_i \frac{\dfrac{hc\nu_i}{k_B T}}{\exp\left(\dfrac{hc\nu_i}{k_B T}\right) - 1} \tag{9}$$

with ν_i denoting the harmonic vibrational frequencies in cm^{-1}, and k_B, the Boltzmann constant. Possible numerical problems caused by low-frequency modes do not appear with the considered molecules; the lowest frequency is about 400 cm^{-1}. Finally, to obtain enthalpies instead of energies, the pressure−volume work term ΔpV has to be added, which is equal to $+RT$ for each mole of gas produced and $-RT$ for each mole consumed, thereby assuming ideal-gas behavior. To obtain a rough estimate for the anharmonicities on the temperature corrections, we calculated the vibrational temperature term also with the fundamental instead of harmonic frequencies (see results).

2.8. Differences to the Original HEAT Protocol. The procedure applied is closest to what has been termed in ref 4 the HEAT345(Q) protocol. However, due to the fact that we consider here systems that contain chlorine, a second-row element, a few modifications were necessary. Those are (1) use of all-electron CCSD(T)/cc-pCVQZ geometries instead of CCSD(T)/cc-pVQZ geometries, thus recognizing the increased

TABLE 4: Various Experimental Results for the Standard Enthalpy of Formation (in kJ/mol) of Vinyl Chloride

ref	method	$\Delta_f H^0$ (298.15 K)
Lacher, Emery, et al., 1956[20,21]	calorimetry hydrogenation	37.2 ± 0.8
Cox and Pilcher, 1970[23]	reanalyzation of data from refs 20, 21	38.1 ± 0.84
Lacher, Gottlieb, et al., 1962[23]	calorimetry	33.8 ± 1.2
Cox and Pilcher, 1970[23]	reanalyzation of data from ref 22	35.3 ± 1.4
Levanova, Treger, et al., 1976[25]	heat of equilibrium	29
Alfassi, Golden, et al., 1973[24]	heat of equilibrium	21
Ritter, 1991[26]	thermochemical network	21.7
Gurvich et al., 1991[27]	reanalyzation	23.0 ± 2.1
Manion, 2002[28]	reanalyzation	22.0 ± 3

importance of a proper treatment of core-correlation effects in the present case; (2) for the same reason, the ZPE corrections have been obtained using the cc-pCV*XZ* basis sets. Furthermore, different from the original HEAT protocol, we split the ZPE term into a harmonic and an anharmonic contributions, which are obtained separately and with different basis sets to keep computational cost at an acceptable level; (3) additional consideration of temperature corrections.

2.9. Computational Details. All calculations have been performed with the Mainz−Austin−Budapest version of ACESII,[57] except those for the RHF-CCSD(T)/aug-cc-pCV5Z energies, which were performed using the MOLPRO package,[58] and those for the CCSDT(Q) energies, which have been carried out using a string-based, many-body code MRCC[7,59] interfaced to ACESII.

Calculations, of which some involved more than 800 basis functions together with up to 34 correlated electrons, were performed on Intel Xeon servers running under the Linux operating system.

3. Results and Discussion

The computed total energies for the species investigated in the present work are summarized in Table 1, together with the individual contributions from eq 1 required for the application of the HEAT scheme. Table 2 then reports the total atomization energies (TAE) for H_2, HCl, Cl_2, C_2H_2, C_2H_4, and CH_2CHCl as they are obtained from the data given in Table 1. Again, we also repeat the individual contributions, and in addition, we compare (for all species except CH_2CHCl) our theoretical atomization energies with those derived within the active thermochemical table (ATcT) of Ruscic and co-workers.[15] This comparison once more confirms the high accuracy that can be achieved with state-of-the-art thermochemical protocols such as HEAT, because the remaining discrepancies between theory and experiment (i.e., the ATcT values) are in all cases below 0.4 kJ/mol.

We note the following: (a) Higher-level correlation energy contributions (HLCEC) are, as is well-known,[2−5] again important. They amount to up to 3−5 kJ/mol (sum of $\Delta E_{\mathrm{CCSDT}}$ and $\Delta E_{\mathrm{CCSDT(Q)}}$) and affect the computed heats of formation by a few kilo-Joules per mole. The effect is particularly pronounced for the systems with multiple bonds, but also nonnegligible for Cl_2. Again, as has been observed before,[5] the CCSDT and CCSDT(Q) contributions to the heats of formation, but not for the total energies, have opposite signs and partially cancel so that the total “beyond CCSD(T)” correction amounts in most cases to <1 kJ/mol. (b) Anharmonic contributions to the ZPE are of the same size as the HLCEC and, thus, important to consider. These corrections are particularly important for the larger systems, that is, C_2H_4 and CH_2CHCl, probably due to the increased number of normal modes. The G_0 contributions to the heats of formation are 0.10, 0.02, 0.00, 0.18, 0.77, and 0.03 kJ/mol for H_2, HCl, Cl_2, C_2H_2, C_2H_4, and CH_2CHCl, respectively, and thus cannot be neglected when aiming at sub-kilo-Joule-per-mole accuracy. (c) Relativistic corrections to the total energies are rather large as soon as the species contains chlorine, but these effects tend to cancel when thermochemical energies are computed. In comparison with results from DKH−CCSD(T) calculations from ref 3, the corrections obtained in a perturbative manner with the mass-velocity and one-electron Darwin terms differ by 0.06, 0.11, 0.02, and 0.01 kJ/mol for the total atomization energy contribution for HCl, Cl_2, C_2H_2, and C_2H_4, respectively. The relativistic effects on the heats of formation are at a few kilo-Joules per mole rather small and of similar magnitude as the HLCEC and the anharmonic corrections to the ZPE. (d) Consideration of spin−orbit corrections is essential, because they amount to ~3.5 kJ/mol per chlorine. For carbon, these corrections are at ~0.35 kJ/mol, significantly smaller, but also not negligible, when aiming at sub-kilo-Joule-per-mole accuracy.

Our theoretical prediction for the atomization energies of H_2, HCl, Cl_2, C_2H_2, and C_2H_4 agree well with previous theoretical high-accuracy values from HEAT or Wn studies.[2−5,60] For CH_2CHCl, our prediction for the atomization energy is 2161.1 kJ/mol.

In Table 3, we compare our calculated standard enthalpies of formation, $\Delta_f H^0$, with available experimental values. Our theoretical values have been obtained from the atomization energies reported in Table 2 using the same standard enthalpies of formation for the atoms at 0 K as in ref 5 (hydrogen, 216.03 kJ/mol; carbon, 711.58 kJ/mol) and a value of 119.62 ± 0.012 kJ/mol from ref 61 for chlorine. We also apply the same scheme to the experimental total atomizations energies. All values for 0 K show excellent agreement, except the values for acetylene and vinyl chloride, wherein a slight disagreement with the numbers in refs 27 and 61 is noted. The ATcT value of 228.82 ± 0.32 kJ/mol from refs 5 is in excellent agreement with our results and shows clearly that the heat of formation given by Gurvich et al. is too low. Assuming similar accuracy for the heat of formation of vinyl chloride at 0 K, we predict a value of 29.79 kJ/mol with a conservative error estimate of ± 1 kJ/mol.

For the enthalpies of formation at a temperature of 298.15 K, we use the CODATA standard enthalpies of formation for the atoms (hydrogen, 217.998 ± 0.006 kJ/mol; carbon, 716.68 ± 0.45 kJ/mol; chlorine, 121.301 ± 0.008 kJ/mol[62]) as well as computed temperature corrections. For the latter, we consider corrections obtained from both the harmonic frequencies and those computed with the fundamental frequencies. We note good agreement for all considered species, with the deviations between theory and experiment in the range of 0.09 to −2.09 kJ/mol. The largest discrepancies are with ~2 kJ/mol, seen for acetylene and ethylene, which is possibly related to the large error bar on the experimental value of the standard enthalpy of formation for the carbon atom. For CH_2CHCl, we thus assume the remaining error in our theoretical prediction of $\Delta_f H^0$(298.15

TABLE 5: Contributions to the Reaction Enthalpies (in kJ/mol) for the Reactions $C_2H_4 + Cl_2 \rightarrow CH_2CHCl + HCl$ (R1) and $C_2H_2 + HCl \rightarrow CH_2CHCl$ (R2)

	R1	R2
E^{∞}_{HF}	−117.08	−117.82
$\Delta E^{\infty}_{\mathrm{CCSD(T)}}$	−0.80	−13.86
$\Delta E_{\mathrm{CCSDT}}$	0.44	0.05
$\Delta E_{\mathrm{CCSDT(Q)}}$	−0.02	0.49
$\Delta E^{\mathrm{harmonic}}_{\mathrm{ZPE}}$	−7.15	24.38
$\Delta E^{\mathrm{anharmonic}}_{\mathrm{ZPE}}$	−0.19	−0.80
ΔE_{REL}	1.21	0.16
ΔE_{SO}	0.00	0.00
ΔE_{DBOC}	−0.16	0.22
$\Delta E^{\mathrm{harmonic}}_{\mathrm{T}}$ (298.15 K)	0.79	−8.16
$\Delta E^{\mathrm{anharmonic}}_{\mathrm{T}}$ (298.15 K)	0.80	−6.76
$\Delta_r H(0K)$	−123.75	−107.18
$\Delta_r H^{\mathrm{harmonic}}$ (298.15 K)	−122.96	−115.34
$\Delta_r H^{\mathrm{anharmonic}}$ (298.15 K)	−122.95	−113.94
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[20,21]	−107.60	−97.20
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[23]	−106.70	−96.30
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[22]	−111.00	−100.66
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[23]	−109.50	−99.10
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[24]	−123.80	−113.40
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[25]	−115.80	−105.40
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[26]	−123.09	−112.69
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[27]	−121.80	−111.40
$\Delta_r H^{0\mathrm{exp}}$ (298.15 K)[28]	−122.80	−112.40

K) to be of a magnitude similar to that for the other investigated species. A conservative estimate, therefore, might be ± 2 kJ/mol. On the other hand, the experimental value for $\Delta_f H^0$(298.15 K) of CH_2CHCl settles in the range of 21.0−38.1 kJ/mol. Our prediction of 20.9 ± 2 kJ/mol supports the values of the upper half of that range and necessarily rejects the others. Table 4 provides a detailed comparison with the experimental values. We note that the values from refs 24, 26, 27, and 28 are consistent with our computations. The value from ref 24 has been determined via the heat of equilibrium, whereas that from ref 26 has been obtained using a thermochemical network, and the values from refs 27 and 28 were found by reinvestigation of the experimental literature. The other values, obtained by either calorimetry or via the heat of equilibrium, are all in absolute terms too high and clearly outside the error bar estimate for our calculated value. In Table 5, we compare our reaction enthalpies for $C_2H_4 + Cl_2 \rightarrow CH_2CHCl + HCl$ and $C_2H_2 + HCl \rightarrow CH_2CHCl$ with the values directly obtained in experiment or derived from the experimental heat of formation of CH_2CHCl. Consistent with our findings for the heat of formation, good agreement is again seen only with the values derived from the values given in refs 24, 26, 27, and 28. The other values[20−23,25] should again be considered unreliable. In Table 5, we also list the individual contributions to the two reaction energies. It is interesting to note that the characteristics of both reactions are rather different. For the first reaction, electron-correlation effects are small (−0.38 kJ/mol), whereas for the second reaction, the latter are, with −13.32 kJ/mol, sizable. For the second reaction, the ZPE effects and the temperature effects are larger, thus rendering an accurate prediction of the reaction enthalpy for this reaction more challenging than for the first. However, our best estimate for those two reactions are −123.0 and −113.9 kJ/mol, with again a conservative error estimate of ±2 kJ/mol.

4. Summary

Using a modified HEAT scheme, the standard heat of formation of CH_2CHCl, $\Delta_f H^0$ is predicted to be 29.79 ± 1 kJ/mol at 0 K and 20.9 ± 2 kJ/mol at 298.15 K. The prediction allows the different experimental values reported for $\Delta_f H^0$(298.15K) to be discriminated and supports those from refs 24, 26, 27 and 28. For the reaction enthalpy of $C_2H_4 + Cl_2 \rightarrow CH_2CHCl + HCl$ and $C_2H_2 + HCl \rightarrow CH_2CHCl$, we obtain using the same theoretical ansatz −123.0 and −113.9 ± 2 kJ/mol, respectively.

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