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One-Electron Reduction of Substituted Chlorinated Methanes As Determined from ab Initio Electronic Structure Theory

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Substituted chloromethyl radicals and anions are potential intermediates in the reduction of substituted chlorinated methanes ($CH_xCl_{3-x}L$, with $L^- = F^-$, OH^-, SH^-, NO_3^-, HCO_3^- and $x = 0-3$). Thermochemical properties, ΔH_f°(298.15 K), S°(298.15 K,1 bar), and ΔG_S(298.15 K, 1 bar), were calculated by using ab initio electronic structure methods for the substituted chloromethyl radicals and anions: $CH_yCl_{2-y}L^\bullet$ and $CH_yCl_{2-y}L^-$, for $y = 0-2$. In addition, thermochemical properties were calculated for the aldehyde, ClHCO, and the *gem*-chlorohydrin anions, CCl_3O^-, $CHCl_2O^-$, and CH_2ClO^-. The thermochemical properties of these additional compounds were calculated because the nitrate-substituted compounds, $CH_yCl_{2-y}(NO_3)^\bullet$ and $CH_yCl_{2-y}(NO_3)^-$, were not stable, with all levels of ab initio theory leading to highly dissociated complexes. On the basis of these thermochemical estimates, the overall reaction energetics (in the gas phase and aqueous phase) for several mechanisms of the first electron reduction of the substituted chlorinated methanes were predicted. In almost all of the cases, the thermodynamically most favorable pathway resulted in loss of Cl^-. The exception was for the reduction of the nitrate-substituted chlorinated methanes $CH_xCl_{3-x}(NO_3)$. On reduction, these compounds were shown to readily decompose into a Cl^- anion, $NO_2^\bullet$ gas, and an aldehyde. In addition, the results of this study suggest that a higher degree of chlorination corresponds to a more favorable reduction. Relative to the nonsubstituted chlorinated methanes, the thermodynamic results suggest the $CH_xCl_{3-x}F$, $CH_xCl_{3-x}OH$, and $CH_xCl_{3-x}(HCO_3)$ compounds are moderately more difficult to reduce, the $CH_xCl_{3-x}SH$ compounds are moderately less difficult to reduce, and the $CH_xCl_{3-x}(NO_3)$ compounds are substantially more favorable to reduce. These results demonstrate that ab initio electronic structure methods can be used to calculate the reduction potentials of organic compounds to help identify the potentially important environmental degradation reactions.

I. Introduction

Polychlorinated alkanes (PCA's), such as carbon tetrachloride, are widespread groundwater pollutants. The potential health risks to the public of the presence of these toxic and carcinogenic chemicals being in the groundwater makes knowing their environmental fate extremely important. One of the key degradation pathways for PCA's in anaerobic groundwater environments is reductive dechlorination (i.e., hydrogenolysis).[104] In this reaction, the addition of two electrons results in release of chloride and the formation of a new C−H bond on the PCA. The two electrons can come from a variety of sources including mineral surfaces,[3,28,69,119] zerovalent metals,[5,6,17,78,111] organic molecules such as quinones,[23,90,91,115] organometallics such as an iron porphyrin complex,[21,74,117] metalloenzymes,[47] or microbes.[60,79] This two electron-transfer process is hypothesized to occur in two sequential steps for $x = 0-2$: the first electron transfer to the PCA is dissociative attachment leading to formation of a chloroalkyl radical and a chloride, reaction 1,

$$R-CH_xCl_{3-x} + 1e^- \rightarrow R-CH_xCl_{2-x}^\bullet + Cl^- \qquad (1)$$

and the second electron transfer allows the newly formed radical to incorporate a proton to form a neutral compound, reaction 2.

$$R-CH_xCl_{2-x}^\bullet + 1e^- + H^+ \rightarrow R-CH_{x+1}Cl_{2-x} \qquad (2)$$

The current consensus is that the first electron transfer (reaction 1) is the rate-limiting step, and several researchers have shown that strong correlations exist between quantities derived from thermodynamic values of the first electron-transfer process and the overall degradation rate.[18,92,102] As a result, accurate thermochemical data for the chloroalkyl radical compounds are needed to understand the degradation of PCA's. Such data also will be useful for understanding the toxicity of PCA's[50,67] and their degradation reactions in biological systems because much of their toxicity can be traced to the formation of chloroalkyl radicals during anaerobic reduction by iron-II containing enzymes.[26,77,100,107,121]

Besides the involvement of radical intermediates, it has been hypothesized that carbanions may play a role in PCA degradation, especially in highly basic environments or with PCA's that have strong electron-withdrawing groups, conjugation, or aromatic groups.[109,125] Furthermore, several groups have hypothesized the formation of carbenes in their studies,[1,3,6,86] and the existence of carbenes in PCA degradation would strongly suggest a 1,1-elimination process with a carbanion intermediate.[57,58,109] However, there is little direct experimental evidence

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to support carbene formation, as well as some evidence against it. A strong argument against carbene formation is that carbanion formation is thermodynamically prohibited in most cases, as the gas-phase electron affinity of chlorine is much higher than that of organic radicals. It is nearly double that of the trichlormethyl radical ($EA(CCl_3^\bullet) = 48$ kcal/mol,[20] $EA(Cl^\bullet) = 83$ kcal/mol[20]).

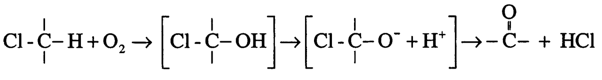
In a previous study, we reported the reaction energies for the chlorinated methanes with several environmentally important aqueous monovalent anions.[19] This previous study showed that it is thermodynamically favorable for several environmentally important anions to displace a chloride. Nucleophilic substitution of Cl^- with OH^-, SH^-, HCO_3^-, and F^- are significantly exothermic, and reactions with NO_3^- are slightly exothermic to thermoneutral, even though most of these reactions are thought to be rather slow in terms of the kinetics.[15,28] The products of these reactions may become important on the reaction time scales relevant to natural groundwater systems, as demonstrated by the presence of sulfide compounds in both laboratory and field studies.[7,52,103] A reasonable assumption is that the one-electron reduction potential of these compounds will be a major factor controlling their degradation rates in groundwater environments, as well as their potential toxicities. However, experimentally determined one-electron reduction potentials are known for only a few of these compounds. In this work, electronic structure methods are used to calculate the thermochemical properties (in the gas phase and aqueous solution) of likely products from a one-electron reduction including the radicals $CCl_3^\bullet$, $CHCl_2^\bullet$, $CH_2Cl^\bullet$, $CCl_2F^\bullet$, $CHClF^\bullet$, $CH_2F^\bullet$, $CCl_2OH^\bullet$, $CHClOH^\bullet$, $CH_2OH^\bullet$, $CCl_2SH^\bullet$, $CHClSH^\bullet$, $CH_2SH^\bullet$, $CCl_2(HCO_3)^\bullet$, $CHCl(HCO_3)^\bullet$, and $CH_2(HCO_3)^\bullet$ and the closed shell anions CCl_3^-, $CHCl_2^-$, CH_2Cl^-, CCl_2F^-, $CHClF^-$, CH_2F^-, CCl_2OH^-, $CHClOH^-$, CH_2OH^-, CCl_2SH^-, $CHClSH^-$, CH_2SH^-, $CCl_2(HCO_3)^-$, $CHCl(HCO_3)^-$, and $CH_2(HCO_3)^-$. By using this thermochemical data, we compare the energetics of four possible pathways for the first one-electron reductive step

$$CH_xCl_{3-x}L + 1e^- \rightarrow \begin{cases} CH_xCl_{2-x}L^\bullet + Cl^- & \text{(pathway 1)} \\ CH_xCl_{3-x}{}^\bullet + L^- & \text{(pathway 2)} \\ CH_xCl_{2-x}L^- + Cl^\bullet & \text{(pathway 3)} \\ CH_xCl_{3-x}{}^- + L^\bullet & \text{(pathway 4)} \end{cases} \tag{3}$$

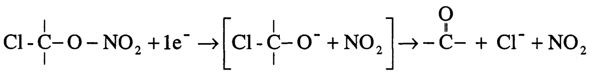
where $L^- = F^-$, OH^-, SH^-, NO_3^-, HCO_3^- and $x = 0-2$.

In addition to the substituted chloromethyl radicals and anions, thermochemical properties were calculated for the aldehyde ClHCO, and the *gem*-chlorohydrin anions CCl_3O^-, $CHCl_2O^-$, and CH_2ClO^-. These additional compounds are possible intermediates of PCA oxidation[4] and are also possible intermediates in the reduction of nitrate-substituted chlorinated methanes. In addition, the *gem*-chlorohydrin anions exhibit novel structures and are relevant to chloride affinity studies.[72,73]

Oxygen and nitrate are capable of opening up reaction pathways other than simple electron-transfer pathways. For example, the oxidation of chlorinated methanes can proceed through the *gem*-chlorohydrin intermediates to form carbonyl derivatives (reaction 4).[4] A very similar pathway for the reduction of nitrate-substituted chlorinated methanes is suggested by a simple oxidation−reduction argument, as shown in reaction 5. The oxidation−reduction line of reasoning is based on the fact that the nitrate-substituted compounds can be more reduced at N than at C, resulting in NO_2 gas and a *gem*-chlorohydrin compound, which further degrades to form a carbonyl derivative. The carbon atom has formal oxidation states of +4, +2, and −2, respectively in the nitrate-substituted compounds, $CCl_3(NO_3)$, $CHCl_2(NO_3)$, and $CH_3(NO_3)$, whereas these compounds have a formal +5 oxidation state on the more electronegative nitrogen atom. Thermochemical properties presented in this work further support these rudimentary oxidation−reduction arguments.



$$Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}H + O_2 \rightarrow \left[Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}OH\right] \rightarrow \left[Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}O^- + H^+\right] \rightarrow -\overset{O}{\overset{\|}{C}}- + HCl \tag{4}$$



$$Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}O-NO_2 + 1e^- \rightarrow \left[Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}O^- + NO_2\right] \rightarrow -\overset{O}{\overset{\|}{C}}- + Cl^- + NO_2 \tag{5}$$

Computational thermochemical approaches based on ab initio electronic structure methods are constantly being developed and improved upon, but these methods are rarely able to give heat of formations in the gas phase of a broad class of molecules with more than a few first or second row atoms with error limits of less than a few kcal/mol.[24,25,96] Only when very large basis sets such as the correlation-consistent basis sets[35] extrapolated to the complete basis set limit, high level treatments of correlation energy such as coupled cluster methods (CCSD(T)),[9,10,70] and small correction factors such as core-valence correlation energies and relativistic effects are included can the heat of formation from ab initio electronic structure methods be predicted to within 1 kcal/mol. Although one can now accurately calculate the heats of formation of molecules with up to six first row atoms, such high-level calculations are extremely demanding and scale computationally as N^7 for N basis functions with large basis sets.[30−34,36−39,41−43,101] In addition to the issues associated with ab initio electronic structure methods, our objective, the prediction of the thermochemical properties of chloroalkyl radical and anionic compounds in solution, also requires that solvation contributions be included in addition to the gas-phase thermodynamic properties of heats of formation and entropies. For example, we have used a supermolecular/continuum solvent-inclusion approach to calculate the absolute free energy of solvation of a proton in water.[126] Patterson et al. have used an approach similar to the one that we use based on density functional theory and a semiempirical approach to including solvent effects to study the reductive dechlorination of hexachloroethane.[86]

The computational methods used in this work are described in section II. Calculations for the enthalpies of formation in the gas phase of $CH_xCl_{2-x}L$, $CH_xCl_{2-x}L^-$, ClHCO, CCl_3O^-, $CHCl_2O^-$, and CH_2ClO^- are reported in section III. The difficulties associated with calculating absolute heats of formation from atomization energies are avoided by using a strategy based on isodesmic reactions. The entropies of gas-phase $CH_xCl_{2-x}L$, $CH_xCl_{2-x}L^-$, ClHCO, CCl_3O^-, $CHCl_2O^-$, and CH_2ClO^- compounds are calculated by using standard statistical mechanical expressions are reported in section IV. The calculations of the solvation energies of the gas-phase $CH_xCl_{2-x}L$, $CH_xCl_{2-x}L^-$, ClHCO, CCl_3O^-, $CHCl_2O^-$, and CH_2ClO^- compounds using the continuum solvation model of Tomasi et al.[22,82] are reported in section V. This treatment of solvation is far more computationally efficient than explicitly doing simulations with water molecules in a supermolecule approach. It has been shown to give solvation energies within a few kcal/mol,[110] which for this study is adequate because the gas-phase enthalpies of formation are predicted to no better than a few kcal/mol. The results from this paper and our previous paper[19] are collected and discussed in section VI to provide estimates of thermodynamic properties for the pathways of one-electron transfer to the substituted and nonsubstituted chlorinated methanes, and concluding remarks are given in section VII.

II. Ab Initio and Continuum Solvation Calculations

All of the ab initio calculations in this study were performed with the Gaussian-98 program suite[46] unless noted below. Tables SM-1−SM-8 of the Supporting Information contain the electronic energies and thermal vibrational energies at 298.15 K for all of the compounds investigated in this study. The gas-phase geometries for the neutral, radical, and anionic species were optimized at each level of theory. The ab initio calculations in this study were performed at the level of density functional theory (DFT)[59] and second-order Møller−Plesset perturbation theory (MP2).[83] The DFT Kohn−Sham equations[68] were solved by using the LDA (local density approximation),[116] BPW91 (Becke-88, Perdew−Wang-91),[12,89] and B3LYP (Becke-3 parameter, Lee, Yang, and Parr)[13,75] exchange-correlation functionals. The DFT calculations were performed by using both the DZVP2[48] basis set and the DZVP2 basis set augmented with diffuse functions (aug-DZVP2). The diffuse functions were generated by using an even-tempered strategy. The Gaussian exponents for the diffuse functions are given in the Supporting Information in Table SM-9. Similarly, MP2 calculations were done by using both the cc-pVDZ[35,93,94,122,123] basis set and the aug-cc-pVDZ[35,93,94,122,123] basis sets. The DZVP2, cc-pVDZ, and aug-cc-pVDZ basis sets were obtained from the Extensible Computational Chemistry Environmental Basis Set Database.[44] When possible, G2[25] calculations were used to confirm the accuracy of our gas-phase enthalpy estimates. The accuracy of this theory, which contains empirical parameters, is quite good, reproducing experimental atomization energies to within a few kcal/mol for many molecules. However, these calculations are computationally very intensive, which limits the size of molecules that can be studied by using this method.

Solvent effects were estimated by using the self-consistent reaction field (SCRF) theory of Tomasi et al,[22,45,82,110] with the cavity defined by the united atom model.[8] SCRF theory can be combined with a variety of ab initio electronic structure routines in the Gaussian-98 program suite, including DFT, with the LDA, BP91, and B3LYP functionals, and MP2. The calculated gas-phase geometries were used in the solvation calculations.

III. Gas-Phase Enthalpies of Formation

The enthalpies of formation for the gas-phase radicals, $CH_xCl_{2-x}L^\bullet$, for $x = 0-2$, were calculated by using an isodesmic strategy based on the hydrogen exchange reaction, the same approach followed by Kumaran et al.[71] for the chloromethyl radicals

$$CH_{x+1}Cl_{2-x}L + CH_3^\bullet \rightarrow CH_xCl_{2-x}L^\bullet + CH_4 \tag{6}$$

This isodesmic reaction is simpler than the isodesmic reactions used by Luke et al.,[77] which have up to six bonds being broken and re-formed. Similarly, the enthalpies of formation for the majority gas-phase anionic $CH_xCl_{2-x}L^-$ compounds considered in this study are calculated by using an isodesmic strategy based on the acidity reaction.

$$CH_{x+1}Cl_{2-x}L + CH_3^- \rightarrow CH_xCl_{2-x}L^- + CH_4 \tag{7}$$

The defining property of an isodesmic reaction (that there are an equal number of like bonds on the left-hand and right-hand sides of the reaction[53]) helps to minimize the error in the reaction energy. These reactions are designed to separate out the interactions between the carbon substituents and nonbonding electrons from the direct bonding interactions by having the direct bonding interactions largely canceling one another. This separation is quite attractive. Most ab initio methods give substantial errors when direct bonding interactions are estimated due to the computational difficulties associated with electron pair correlation, whereas ab initio methods are expected to be more accurate for estimating neighboring interactions and long-range through-bond effects. Not withstanding these rationalizations, the reliability of the isodesmic calculations based on eqs 6 and 7 may be limited due to changes in structure, as well as the shape of the radical electron (electron pair), as the degree of chlorination is increased from $CH_3^\bullet$ (CH_3^-) to $CH_xCl_{2-x}^\bullet$ ($CH_xCl_{2-x}^-$) compounds. For example, the structure for $CH_3^\bullet$ is planar and the structure for $CCl_3^\bullet$ is pyramidal. In addition, the geometries for the anions may show significant changes due to formation of strongly hydrogen-bonded complexes of Cl^- with a concomitant loss of the C−Cl bond. These differences in shape may reduce the cancellation of errors that is sought in the isodesmic strategy. However, the accuracy obtained previously by Kumaran et al.[71] as well as other researchers,[105,108] implies that the changes in shape of the radical electron (electron pair) are reasonably characterized by the lower level ab initio calculations used in this study.

Geometry optimization calculations for $CH_xCl_{2-x}(NO_3)^\bullet$ and $CH_xCl_{2-x}(NO_3)^-$ led to complexes with long $CO-NO_2$ bonds. This result suggested that we should study the thermodynamics of the reduction mechanism shown in reaction 5. To do this we need to know the heats of formation for the *gem*-chlorohydrin anions, Cl_3CO^-, HCl_2CO^-, and H_2ClCO^-, as well as the aldehydes, Cl_2CO, HClCO, and H_2CO. Accurate heats of formation are known experimentally for Cl_3CO^-, Cl_2CO, and H_2CO compounds, whereas the heats of formation of the remaining compounds can be estimated using isodesmic approaches. Given the known heats of formation for Cl_2CO and H_2CO, the heat of formation of formyl chloride, ClHCO, can readily be estimated using the isodesmic reaction

$$H_2CO + Cl_2CO \rightarrow 2ClHCO \tag{8}$$

To estimate the heat of formation of HCl_2CO^- and H_2ClCO^- the isodesmic reactions

$$Cl_3CO^- + HClCO \rightarrow Cl_2CO + Cl^- \cdots HClCO \tag{9}$$

$$Cl_3CO^- + H_2CO \rightarrow Cl_2CO + Cl^- \cdots H_2CO \tag{10}$$

are used, as the heats of formation of Cl_3CO^-, H_2CO, and Cl_2CO are known experimentally, along with the heat of formation of HClCO obtained from eq 8. The reliability of the isodesmic approach proposed in eqs 9 and 10 may be problematic due to their loosely bound structures. As shown in Figure 1, the optimized structures for HCl_2CO^- and H_2ClCO^- show that these are dissociated complexes with a chloride loosely bound to an aldehyde. Also shown in Figure 1, the optimized structure for Cl_3CO^- is somewhat akin to these structures, but the bonding in Cl_3CO^- contains three bound chlorines rather than just one loosely hydrogen bonded chloride anion as found in HCl_2CO^- and H_2ClCO^-.

After the isodesmic reaction energies are determined at a consistent level of theory, the enthalpies of formation of the unknown $CH_xCl_{2-x}L^\bullet$, $CH_xCl_{2-x}L^-$, ClHCO, HCl_2CO^-, and H_2ClCO^- compounds were calculated using Hess's law (eqs 11−15).

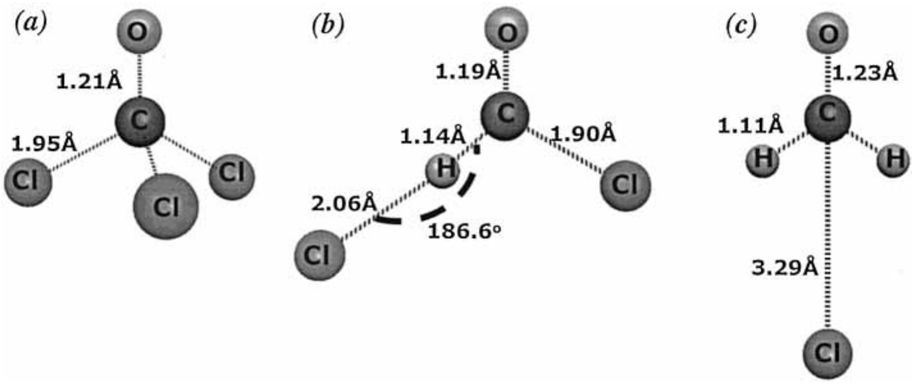


Figure 1. Gas-phase optimized structures at the MP2/aug-cc-pVDZ level for (a) Cl_3CO^-, (b) Cl_2HCO^-, and (c) ClH_2CO^-.

$$\Delta H_f(CH_xCl_{2-x}L^\bullet) = \Delta H_f(CH_3^\bullet)(exp) + \Delta H_f(CH_{x+1}Cl_{2-x}L)(exp) - \Delta H_f(CH_4)(exp) + \Delta H_r(isodesmic) \quad (11)$$

$$\Delta H_f(CH_xCl_{2-x}L^-) = \Delta H_f(CH_3^-)(exp) + \Delta H_f(CH_{x+1}Cl_{2-x}L)(exp) - \Delta H_f(CH_4)(exp) + \Delta H_r(isodesmic) \quad (12)$$

$$\Delta H_f(HClCO) = \Delta H_f(H_2CO)(exp) + \Delta H_f(Cl_2CO)(exp) + \Delta H_r(isodesmic) \quad (13)$$

$$\Delta H_f(HCl_2CO^-) = \Delta H_f(Cl_3CO^-)(exp) + \Delta H_f(HClCO)\ (eq\ 13) - \Delta H_f(Cl_2CO)(exp) + \Delta H_r(isodesmic) \quad (14)$$

$$\Delta H_f(H_2ClCO^-) = \Delta H_f(Cl_3CO^-)(exp) + \Delta H_f(H_2CO)\ (exp) - \Delta H_f(Cl_2CO)(exp) + \Delta H_r(isodesmic) \quad (15)$$

The "known" heats of formation of the other three compounds were obtained from experiment or other calculated values. This strategy for calculating heats of formation is computationally tractable and is expected to be accurate to within a few kcal/mol. This method is simple to apply as long as selected enthalpies of formation (those for $CH_3^\bullet$, CH_3^-, CH_4, $CH_xCl_{3-x}L$, Cl_2CO, H_2CO, and Cl_3CO^-) are known. However, the required enthalpies of formation are available either from experiment or from high-quality ab initio estimates from our previous study.[19]

The gas-phase enthalpies of formation for $CH_xCl_{2-x}L^\bullet$, $CH_xCl_{2-x}L^-$, ClHCO, and $CH_xCl_{3-x}O^-$ are reported in Table 1. The first five columns of this table contain the ΔH_f°(298.15 K) values for the radical compounds (anionic compounds) based on the isodesmic approach using the MP2/cc-pVDZ (MP2/aug-cc-pVDZ), LDA/DZVP2 (LDA/aug-DZVP2), BP91/DZVP2 (BP91/aug-DZVP2), B3LYP/DZVP2 (B3LYP/aug-DZVP2), and G2 approaches with the G2 heats of formation given in the last column. The various ab intio thermal and vibrational energies at 298.15 K used to calculate isodesmic reaction energies are given as Supporting Information, and experimental and high-quality ab initio values needed to evaluate eqs 11−15 are given in Table A1 of the Appendix. For the radical compounds, the average absolute differences from MP2/cc-pVDZ were 5.58, 2.87, 1.53, 1.18, and 0.86 kcal/mol for the LDA/DZVP2, BP91/DZVP2, B3LYP/DZVP2, G2 isodesmic, and G2 atomization methods, respectively, whereas for anionic compounds the average absolute differences from MP2/aug-cc-pVDZ were 2.28, 4.38, 4.39, 2.27, and 1.51 kcal/mol for the LDA/aug-DZVP2, BP91/aug-DZVP2, B3LYP/aug-DZVP2, G2 isodesmic, and G2 atomization methods, respectively.

As expected, the calculated heats of formation between the different ab initio methods are similar with differences on the order of a few kcal/mol. We note that for the $CH_xCl_{2-x}L^\bullet$ compounds the largest difference from the MP2 values are at the LDA level, whereas for the $CH_xCl_{2-x}L^-$, ClHCO, and $CH_xCl_{3-x}O^-$ compounds the largest differences from the MP2 values are at the BP91 level. The worst-case difference was ~10 kcal/mol, and it is between the MP2/aug-cc-pVDZ and B3LYP/aug-DZVP2 calculations for $CHClSH^-$. The good agreement of the MP2 values with the G2 values shows that the former is a good method for cost-effective calculations of heats of formation based on an isodesmic scheme. Additional insight into the accuracy of the isodesmic scheme can be seen in Table 2, where the enthalpies of formations calculated by using the MP2 and G2 isodesmic schemes are compared with available experimental values. The calculated MP2 and G2 isodesmic values are always within 3 kcal/mol of at least one reported experimental value, consistent with previous theoretical studies.[29,71]

IV. Gas-Phase Entropies

Given the structures and vibrational frequencies for a gas-phase molecule, one can calculate its entropy by using formulas derived from statistical mechanics.[55,56,81] Results from these entropy formulas with accurate structures and frequencies will often provide more accurate values than those determined by direct thermal measurements. The situation is more complicated for loosely bound molecules and clusters, because they are likely to have significant coupling between the rotational and vibrational degrees of freedom, and vibrational motion that is not well described by normal vibrations. Estimating accurate entropies in this situation can be a computationally very demanding task, requiring a full intermolecular potential for the molecule, and then sampling over millions of configurations.[66]

Table 3 lists calculated values of S° at 298.15 K for the gas-phase $CH_xCl_{2-x}L^\bullet$, $CH_xCl_{2-x}L^-$, CCl_2CO, HClCO, H_2CO, $NO_2^\bullet$, and $CH_xCl_{3-x}O^-$ compounds considered in this study. Excellent agreement is found between the calculated values and the known experimental values with errors not exceeding 1 cal/(mol K) ($(T\Delta S) < 0.5$ kcal/mol at $T \sim 300$ K). Reported entropy estimates for the anionic compounds are not expected to be as accurate for the neutral compounds, because many of them are loosely bound molecules. As expected, the largest variations in the calculated entropies are for the $CHCl_2O^-$ and CH_2ClO^- *gem*-chlorohydrins that are loosely bound. However, given the difficulty associated with calculating the partition function including full anharmonicity, these are the best available.

The values of ΔH_f and S° in Tables 1 and 3 can be used to calculate ΔG_f° at 298.15 K for the gas phase. This can be done

TABLE 1: Gas-Phase Standard Enthalpies of Formation in kcal/mol from Isodesmic Reactions and Gas-Phase Enthalpies of Formation Estimates Based on Atomization Energies Calculated at the G2 Level[a]

	ΔH_f°(298.15 K) (isodesmic)					ΔH_f°(298.15 K) (atomization)
radicals	MP2/cc-pVDZ	LDA/DZVP2	BP91/DZVP2	B3LYP/DZVP2	G2	G2
$CCl_3^\bullet$	18.42	11.57	14.54	16.12	17.15	17.45
$CHCl_2^\bullet$	23.50	16.68	20.42	21.82	21.82	21.74
$CH_2Cl^\bullet$	28.40	24.66	27.19	28.10	27.61	27.63
$CH_3^\bullet$						35.17
$CCl_2F^\bullet$	−21.75	−27.48	−25.07	−23.30	−21.84	−23.50
$CHClF^\bullet$	−15.64	−20.64	−17.74	−16.19	−15.18	−16.69
$CH_2F^\bullet$	−7.54	−10.71	−8.39	−7.36	−6.35	−7.58
$CCl_2OH^\bullet$	−20.60	−26.83	−24.13	−22.45	−22.21	−21.40
$CHClOH^\bullet$	−12.45	−18.24	−14.93	−13.33	−8.38	−12.20
$CH_2OH^\bullet$	−4.04	−8.56	−5.59	−4.61	−3.36	−3.65
$CCl_2SH^\bullet$	29.30	22.44	26.11	27.82	28.76	29.72
$CHClSH^\bullet$	35.24	27.68	31.45	33.01	33.68	34.71
$CH_2SH^\bullet$	40.12	33.80	36.41	37.28	38.26	39.84
$CCl_2(HCO_3)^\bullet$	−104.89	−112.49	−109.55	−107.84	−106.20	−104.63
$CHCl(HCO_3)^\bullet$	−101.37	−107.89	−105.12	−103.55	−102.01	−100.51
$CH_2(HCO_3)^\bullet$	−96.37	−101.96	−99.97	−98.70	−96.05	−98.56
$ClHCO$	−45.01	−45.99	−46.18	−45.57	−44.57	−45.78
Cl_2CO						−54.91
H_2CO						−27.80
$NO_2^\bullet$						7.42

	ΔH_f°(298.15 K) (isodesmic)					ΔH_f°(298.15 K) (atomization)
anions	MP2/aug-cc-pVDZ	LDA/aug-DZVP2	BP91/aug-DZVP2	B3LYP/aug-DZVP2	G2	G2
CCl_3^-	−29.75	−29.25	−36.57	−35.97	−31.51	−30.64
$CHCl_2^-$	−9.30	−7.30	−12.86	−13.67	−11.27	−10.79
CH_2Cl^-	13.18	15.30	11.96	11.05	11.21	11.80
CH_3^-						34.02
CCl_2F^-	−69.32	−69.21	−76.68	−76.46	−70.71	−71.80
$CHClF^-$	−41.53	−40.14	−45.59	−46.45	−43.09	−44.30
CH_2F^-	−11.66	−11.57	−14.06	−14.09	−13.00	−13.65
CCl_2OH^-	−63.30	−63.83	−70.65	−70.95	−65.67	−64.29
$CHClOH^-$	−33.37	−33.05	−39.12	−40.38	−31.51	−34.77
CH_2OH^-	0.52	0.23	−1.36	−1.00	−0.75	−0.48
CCl_2SH^-	−13.04	−14.61	−18.46	−17.94	−15.93	−14.40
$CHClSH^-$	12.67	6.03	2.04	1.81	7.76	9.35
CH_2SH^-	27.14	26.15	26.12	26.79	24.81	26.96
$CCl_2(HCO_3)^-$	−152.60	−152.73	−158.52	−158.31	−155.16	−153.03
$CHCl(HCO_3)^-$	−136.41	−135.68	−140.46	−140.96	−144.20	−142.13
$CH_2(HCO_3)^-$	−111.78	−113.88	−115.51	−114.80	−114.00	−111.94
CCl_3O^-						−122.72
$CHCl_2O^-$	−115.84	−112.16	−117.96	−119.61	−118.68	−117.86
CH_2ClO^-	−90.28	−86.89	−90.76	−93.51	−93.80	−93.40
CH_3O^-						−32.49

[a] Experimental and ab initio total energy values used to determine these enthalpies of formation are given in the Appendix and as Supporting Information. All quantities are in kcal/mol. See text for definitions of isodesmic exchange reactions.

by calculating the entropy of formation, ΔS°_f, found by subtracting off the entropies of the atomic standard states (Table A3) from the virtual entropy of the compounds. For example, $\Delta S^\circ_f(CCl_3^\bullet)$ and $\Delta G_f^\circ(CCl_3^\bullet)$ are calculated from the following expressions:

$$\Delta S_f^\circ(CCl_3^\bullet) = S^\circ(CCl_3^\bullet) - (S^\circ(\text{C-graphite}) + 3S^\circ({}^1/_2Cl_2)) \tag{16}$$

$$\Delta G_f^\circ(CCl_3^\bullet) = \Delta H_f^\circ(CCl_3^\bullet) - T\Delta S_f^\circ(CCl_3^\bullet) \tag{17}$$

By using the MP2/cc-pVDZ values for $S^\circ(CCl_3^\bullet)$ and $\Delta H_f^\circ(CCl_3^\bullet)$ (isodesmic), the entropy of formation is calculated to be $\Delta S_f^\circ(CCl_3^\bullet) = -13.30$ cal/(mol K) and the Gibbs free energy of formation is calculated to be $\Delta G_f^\circ(CCl_3^\bullet) = 22.39$ kcal/mol, compared to the experimental values of $\Delta S_f^\circ(CCl_3^\bullet) = -12.43$ cal/(mol K)[20,80,112] and $\Delta G_f^\circ(CCl_3^\bullet) = -22.71$ kcal/mol (using $\Delta H_f^\circ(CCl_3^\bullet) = 19.00$ kcal/mol[20,80,112]), respectively.

V. Solvation Energies

Table 4 lists the free energies of solvation calculated using SCRF theory[8,22,45,82,110,] at various electronic structure levels for the radical, and anionic compounds. These calculations were performed by using gas-phase geometries, and corrections due to changes in internal vibration and rotation were neglected. A basic assumption in our calculations is that the bonding relations within the radical $CH_xCl_{2-x}L^\bullet$ and anionic $CH_xCl_{2-x}L^-$ compounds do not change substantially when going from the gas phase to the solution phase, and thus the corrections for changes in internal vibrations are also neglected. However, this assump-

TABLE 2: Enthalpies of Formation in kcal/mol from Experiment and Isodesmic Calculations

compd	ΔH_f°	method
$CCl_3^\bullet$	17.00	exp^{62,112}
	19.00	exp^{20,80,112}
	19.12	exp^{51,112}
	18.00	exp^{61,112}
	14.10	exp^{112,118}
	18.42	isodesmic/MP2/cc-pVDZ
	17.15	isodesmic/G2
$CHCl_2^\bullet$	21.27	exp^{105,112}
	23.49	exp^{112,114}
	22.30	exp^{61,112}
	25.81	exp^{112,120}
	28.20	exp^{80,112}
	23.50	isodesmic/MP2/cc-pVDZ
	21.82	isodesmic/G2
$CH_2Cl^\bullet$	28.04	exp^{105,112}
	27.72	exp^{61,112}
	29.16	exp^{112,114}
	31.31	exp^{120,112}
	24.14	exp^{80,112}
	28.40	isodesmic/MP2/cc-pVDZ
	27.61	isodesmic/G2
$CCl_2F^\bullet$	−25.10	exp^{51,112}
	−22.94	exp^{80,112}
	−22 ± 2	exp^{27}
	−21.75	isodesmic/MP2/cc-pVDZ
	−21.84	isodesmic/G2
$CHClF^\bullet$	−14.51	exp^{114}
	−15 ± 2	exp^{27}
	−15.64	isodesmic/MP2/cc-pVDZ
	−15.18	isodesmic/G2
$CH_2F^\bullet$	−7.65	exp^{51,80,95,112}
	−8 ± 2	exp^{27}
	−7.54	isodesmic/MP2/cc-pVDZ
	−6.35	isodesmic/G2
$CH_2OH^\bullet$	−2 ± 1	exp^{2,113}
	−4.04	Isodesmic/MP2/cc-pVDZ
	−3.36	Isodesmic/G2
CCl_3^-	−33.1 ± 2.2	exp^{2,88}
	−33.06	exp^{2,88}
	−33.7 ± 6.2	exp^{2,14}
	−29.75	isodesmic/MP2/aug-cc-pVDZ
	−30.73	isodesmic/G2
$CHCl_2^-$	−14.1 ± 3.2	exp^{2,14}
	−12.9 ± 2.3	exp^{2,16}
	−9.30	isodesmic/MP2/aug-cc-pVDZ
	−10.89	isodesmic/G2
CH_2Cl^-	10.7 ± 3.2	exp^{2,63}
	15.85	exp^{2,97}
	13.18	isodesmic/MP2/aug-cc-pVDZ
	11.06	isodesmic/G2
CCl_2F^-	−72.36	exp^{2,87}
	−72.7 ± 2.2	exp^{2,98}
	−73.56	exp^{2,98}
	−69.32	isodesmic/MP2/aug-cc-pVDZ
	−70.71	isodesmic/G2
$CHClF^-$	−41.8 ± 2.2	exp^{2,98}
	−41.53	isodesmic/MP2/aug-cc-pVDZ
	−43.09	isodesmic/G2
CH_2F^-	−12.7 ± 4.5	exp^{2,49}
	−11.66	isodesmic/MP2/aug-cc-pVDZ
	−13.00	isodesmic/G2
CH_2SH^-	24.1 ± 2.7	exp^{2,65}
	27.14	isodesmic/MP2/aug-cc-pVDZ
	24.81	isodesmic/G2

tion may create sizable errors for the $CH_xCl_{3-x}O^-$ compounds, depending on the degree to which these compounds dissociate in solution.

Calculated SCRF free energies of solvation cannot be compared directly to thermodynamic tables, because they use different standard states. The standard states for the SCRF model are 1 mol/L at 298.15 K in the gas phase and 1 M at 298.15 K in the solution phase. Thermodynamics tables on the other hand define the standard state for the solute as 1 bar of pressure at 298.15 K in the gas phase and 1 M 298.15 K in the solution phase. In order for the SCRF theory calculations to conform to the standard state of 1 bar of pressure at 298.15 K in the gas phase, a constant value of 1.90 kcal/mol must be added to the SCRF free energies of solvation. For charged solutes, comparisons are less straightforward. Thermodynamic tables report free energies of formation for charged solutes or electrolytes in solution relative to $H^+(aq)$, with the convention that the free energy of formation of the solvated proton is zero at every temperature.[76,118]

$$\Delta G_f^\circ(H^+(aq)) = 0 \tag{18}$$

This means that the absolute solvation free energy of a charged solute cannot be calculated by using thermodynamic tables. However, if the true free energy of the hydrogen electrode process

$$\frac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-(g) \qquad \Delta G_{rxn} = -E_H^\circ \tag{19}$$

is known, then the solvation energy of a charged solute at 298.15 K can be found by subtracting the absolute free energy of the hydrogen electrode process, i.e.,

$$\Delta G_s(X^-) = \Delta G_f^\circ(X(aq)^-) - \Delta G_f^\circ(X(g)^-) + \left\{-E_H^\circ - \left(\Delta G_f^\circ(H(aq)^+) + \Delta G_f^\circ(e(g)^-) - \frac{1}{2}\Delta G_f^\circ(H_2(g))\right)\right\} \tag{20}$$

Similarly, SCRF calculated solvation energies, $\Delta G_{SCRF}(X^-)$, can be used to calculate the free energies of formation $\Delta G_f^\circ(X^-(aq))$ at 298.15 K in the electrolyte standard state used by thermodynamic tables.[86]

$$\Delta G_f^\circ(X(aq)^-) = \Delta G_{SCRF}(X^-) + \Delta G_f^\circ(X(g)^-) - \left\{-E_H^\circ - \left(\Delta G_f^\circ(H(aq)^+) + \Delta G_f^\circ(e(g)^-) - \frac{1}{2}\Delta G_f^\circ(H_2(g))\right)\right\} \tag{21}$$

The exact value for E_H° remains unknown despite extensive experimental and computational efforts. However, Zhan and Dixon[126] have recently performed a first-principles determination of the related value of $\Delta G_{hyd}(H^+)$ at 298.15 K

$$H(g)^+ \rightarrow H(aq)^+ \tag{22}$$

TABLE 3: Calculated Values of Gas-Phase Standard Virtual Molar Entropies ($S°$, cal mol^{-1} K^{-1})

compounds	sym	MP2/cc-pVDZ	LDA/DZVP2	BP91/DZVP2	B3LYP/DZVP2
			Radicals		
$CCl_3^{\bullet}$ [a]	(C_{3v})	71.61	71.99	72.19	72.12
$CHCl_2^{\bullet}$	(C_{2v})	63.53	63.56	63.71	63.66
$CClH_2^{\bullet}$	(C_{2v})	57.05	58.68	60.54	61.80
$CH_3^{\bullet}$ [a]	(D_{3h})	46.69	46.56	46.61	46.54
$CCl_2F^{\bullet}$	(C_s)	71.03	71.29	71.55	71.35
$CHClF^{\bullet}$	(C$_1$)	63.96	64.14	64.24	64.14
$CH_2F^{\bullet}$	(C_s)	56.11	56.87	56.51	56.41
$CCl_2OH^{\bullet}$	(C_s)	71.09	71.43	71.678	71.48
$CHClOH^{\bullet}$	(C_1)	65.51	66.03	66.15	65.99
$CH_2OH^{\bullet}$	(C_1)	57.08	57.90	57.57	57.49
$CCl_2SH^{\bullet}$	(C_1)	75.93	78.11	78.07	78.08
$CHClSH^{\bullet}$	(C_1)	69.34	70.29	70.19	69.86
$CH_2SH^{\bullet}$	(C_s)	61.37	63.56	60.59	60.51
$CCl_2(HCO_3)^{\bullet}$	(C_s)	87.46	88.05	88.86	88.24
$CHCl(HCO_3)^{\bullet}$	(C_1)	81.77	81.56	82.41	82.05
$CH_2(HCO_3)^{\bullet}$	(C_s)	73.03	73.90	72.86	72.60
			Miscellaneous		
Cl_2CO [a]	(C_{2v})	67.60	67.75	68.02	67.82
HClCO	(C_s)	61.87	61.95	62.10	61.97
H_2CO [a]	(C_{2v})	52.27	52.33	52.34	52.28
$NO_2^{\bullet}$ [a]	(C_{2v})	57.38	57.47	57.57	57.46

compounds	sym	MP2/aug-cc-pVDZ	LDA/aug-DZVP2	BP91/aug-DZVP2	B3LYP/aug-DZVP2
			Anions		
CCl_3^-	(C_{3v})	72.20	72.88	73.98	73.48
$CHCl_2^-$	(C_{2v})	65.46	65.64	66.34	66.27
$CClH_2^-$	(C_{2v})	56.79	56.78	57.12	57.20
CH_3^-	(C_{3v})	46.31	46.39	46.31	46.27
CCl_2F^-	(C_s)	72.05	72.46	73.57	73.23
$CHClF^-$	(C_1)	64.26	64.23	64.89	64.88
CH_2F^-	(C_s)	55.29	55.14	55.36	55.29
CCl_2OH^-	(C_s)	73.64	74.17	75.85	75.85
$CHClOH^-$	(C_1)	66.77	65.68	66.76	67.42
CH_2OH^-	(C_1)	56.58	56.58	56.81	56.587
CCl_2SH^-	(C_s)	75.59	75.70	77.21	76.61
$CHClSH^-$	(C_1)	73.17[b]	68.31[b]	69.13[b]	69.20[b]
CH_2SH^-	(C_s)	59.48	61.26	59.60	59.54
$CCl_2(HCO_3)^-$	(C_s)	88.12	88.37	90.30	89.21
$CHCl(HCO_3)^-$	(C_1)	81.27	81.75	82.73	82.15
$CH_2(HCO_3)^-$	(C_s)	72.71	72.15	72.95	72.74
CCl_3O^-	(C_s)	79.15	79.23	80.53	80.10
$CHCl_2O^-$	(C_1)	71.62[b]	73.66[b]	75.67[b]	71.84[b]
CH_2ClO^-	(C_{2v})	73.63[b]	65.68[b]	68.08[b]	72.35[b]
CH_3O^-	(C_{3v})	52.81	52.81	52.84	52.79

[a] Known experimental entropies:[20] $S°(CCl_3) = 70.94$, $S°(CH_3) = 46.41$, $S°(Cl_2CO) = 67.83$, $S°(H_2CO_3) = 52.33$, $S°(NO_2) = 57.37$. [b] Entropy estimates are expected to be less accurate, as these are partially dissociated molecules.

by using the latest developments in electronic structure theory including solvation effects. In this work, high-level ab initio electronic structure calculations were performed by using a supermolecule-continuum approach. In the supermolecule-continuum approach, part of the solvent surrounding the solute was treated quantum mechanically and an SCRF model approximated the remaining bulk solvent. With this approach, the calculated results can systematically be improved by increasing the number of quantum mechanically treated solvent molecules. $\Delta G_{hyd}(H^+)$ at 298.15 K was calculated to be −262.4 kcal/mol, giving an E_H° value of 101.7 kcal/mol at 298.15 K, based on the following equation.

$$\begin{aligned} E_H^\circ &= \Delta G_{hyd}(H^+) + (\Delta G_f^\circ(H(g)^+) - \Delta G_f^\circ(H_2(g))) \\ &= -262.4 \text{ kcal mol}^{-1} + 364.1 \text{ kcal mol}^{-1} \\ &= 101.7 \text{ kcal mol}^{-1} \end{aligned} \quad (23)$$

Using this value along with the values of $\Delta G_f^\circ(H^+(aq))$, $\Delta G_f^\circ(e^-(g))$, and $\Delta G_f^\circ(H_2(g))$, we can simplify eqs 20 and 21 as

$$\Delta G_s(X^-) = \Delta G_f^\circ(X(aq)^-) - \Delta G_f^\circ(X(g)^-) - 101.7 \text{ kcal mol}^{-1} \quad (20b)$$

$$\Delta G_f^\circ(X(aq)^-) = \Delta G_{SCRF}(X^-) + \Delta G_f^\circ(X(g)^-) + 101.7 \text{ kcal mol}^{-1} \quad (21b)$$

VI. Energetics of the First One-Electron Reductive Step

With all of the calculated values described above, we can estimate the thermochemical properties of likely products from a one-electron reduction of PCA's. As discussed in the Introduction, the $\Delta H_f^\circ(CH_xCl_{2-x}L^{\bullet}(g))$, $\Delta H_f^\circ(CH_xCl_{2-x}L^-(g))$, and $\Delta H_f^\circ(HClCO(g))$ values in Table 1 can be used to calculate the gas-phase energetics for the reduction mechanisms shown in eq 1, for $L^- = SH^-$, HCO_3^-, OH^-, F^-, and NO_3^-. In reporting the gas-phase energetics for the reduction of the nitrate-substituted compounds, $CH_xCl_{3-x}(NO_3)$, the products are taken to be an aldehyde, Cl^-, and $NO_2^{\bullet}$ (see eq 5). The results of these calculations are shown in Table 5 and are based on the isodesmic MP2 values for $\Delta H_f^\circ(CH_xCl_{2-x}L^{\bullet}(g))$, ΔH_f°-

TABLE 4: SCRF Calculated Free Energies (ΔG_{SCRF}) of Solvation (kcal/mol)[a]

compounds	MP2/cc-pVDZ	LDA/DZVP2	BP91/DZVP2	B3LYP/DZVP2
		Radicals		
$CCl_3^{\bullet}$	4.30	4.44	4.68	4.60
$CHCl_2^{\bullet}$	1.04	1.86	1.91	1.85
$CClH_2^{\bullet}$	1.29	1.81	1.71	1.66
$CH_3^{\bullet}$	3.50	3.42	3.38	3.40
$CCl_2F^{\bullet}$	3.72	4.04	4.15	4.03
$CHClF^{\bullet}$	−0.02	0.58	0.66	0.50
$CH_2F^{\bullet}$	0.79	1.03	1.03	0.86
$CCl_2OH^{\bullet}$	−2.35	−2.91	−2.30	−2.40
$CHClOH^{\bullet}$	−5.47	−5.93	−5.23	−5.39
$CH_2OH^{\bullet}$	−2.95	−4.16	−3.44	−3.53
$CCl_2SH^{\bullet}$	2.27	2.36	2.60	2.59
$CHClSH^{\bullet}$	−0.87	−0.87	−0.51	−0.46
$CH_2SH^{\bullet}$	0.18	−0.20	0.13	0.21
$CCl_2(HCO_3)^{\bullet}$	−4.13	−3.56	−2.59	−2.71
$CHCl(HCO_3)^{\bullet}$	−6.18	−6.04	−5.22	−5.74
$CH_2(HCO_3)^{\bullet}$	−5.33	−5.36	−4.62	−5.00
		Miscellaneous		
Cl_2CO	3.02	3.37	3.56	3.36
$HClCO$	−0.27	0.46	0.71	0.38
H_2CO	−0.07	0.67	0.76	0.42
$NO_2^{\bullet}$	1.77	2.55	2.63	2.52
$Cl^{\bullet}$	3.16	5.76	3.47	3.17
$F^{\bullet}$	3.02	3.28	2.98	2.97
$OH^{\bullet}$	−2.76	−3.25	−3.02	−3.15
$SH^{\bullet}$	1.50	0.45	1.50	1.54
$HCO_3^{\bullet}$	−11.49	−7.16	−6.17	−6.15
$NO_3^{\bullet}$	1.63	2.82	2.92	2.72
compounds	MP/aug-cc-pVDZ	LDA/aug-DZVP2	BP91/aug-DZVP2	B3LYP/aug-DZVP2
		Anions		
CCl_3^-	−48.88	−49.07	−47.52	−47.89
$CHCl_2^-$	−55.28	−56.13	−54.66	−54.67
$CClH_2^-$	−66.64	−65.87	−65.40	−65.29
CH_3^-	−78.89	−75.51	−75.48	−75.98
CCl_2F^-	−51.15	−51.42	−49.73	−49.82
$CHClF^-$	−60.52	−60.54	−59.43	−59.54
CH_2F^-	−74.93	−72.60	−72.77	−73.47
CCl_2OH^-	−56.76	−57.23	−56.83	−56.81
$CHClOH^-$	−65.54	−65.83	−62.96	−64.94
CH_2OH^-	−79.10	−77.59	−77.26	−77.48
CCl_2SH^-	−51.48	−51.28	−50.53	−50.67
$CHClSH^-$	−62.81	−57.92	−57.13	−57.27
CH_2SH^-	−66.37	−64.20	−65.41	−65.79
$CCl_2(HCO_3)^-$	−55.00	−55.51	−53.46	−53.72
$CHCl(HCO_3)^-$	−58.72	−58.72	−56.91	−56.56
$CH_2(HCO_3)^-$	−64.93	−63.43	−62.38	−63.30
CCl_3O^-	−49.15	−46.40	−45.96	−47.13
$CHCl_2O^-$	−55.26	−52.24	−51.72	−53.21
CH_2ClO^-	−61.90	−61.80	−60.94	−59.83
CH_3O^-	−89.93	−86.16	−83.96	−83.39
Cl^-	−74.86	−73.45	−73.89	−73.80
F^-	−104.30	−100.04	−100.39	−101.12
OH^-	−103.32	−99.02	−98.47	−99.63
SH^-	−70.59	−69.45	−69.74	−69.56
HCO_3^-	−72.66	−70.76	−69.80	−70.95
NO_3^-	−61.53	−60.82	−60.60	−60.85

[a] In order for the SCRF theory calculations to conform to the standard state of 1 bar of pressure at 298.15 K in the gas phase, a constant value of 1.90 kcal/mol was added to the SCRF free energies of solvation.

($CH_xCl_{2-x}L^-$(g)), and ΔH_f°(HClCO(g)). The MP2 values, as discussed in section III, agree well with available experimental values and are expected to be good estimates. The remaining values needed to generate Table 5 can be found in Table A1, which contains experimental and high-quality ab initio values for $\Delta H_f^{\circ}(L^-(g))$, $\Delta H_f^{\circ}(Cl^-(g))$, $\Delta H_f^{\circ}(L^{\bullet}(g))$, $\Delta H_f^{\circ}(Cl^{\bullet}(g))$, $\Delta H_f^{\circ}(NO_2^{\bullet}(g))$, $\Delta H_f^{\circ}(Cl_2CO(g))$, $\Delta H_f^{\circ}(H_2CO(g))$, $\Delta H_f^{\circ}(CH_xCl_{3-x}L(g))$, and $\Delta H_f^{\circ}(e^-(g))$. As expected, pathway 1 is the lowest energy pathway for all of the compounds considered in this study. The next most favorable pathway is pathway 2. However, for most of the compounds studied, this pathway is not favorable, with the only exceptions being for the $CH_xCl_{3-x}(HCO_3)$ compounds and the nitrates. Finally, pathways 3 and 4 are predicted to be very unlikely pathways.

For the most part the reduction of the substituted chlorinated methanes is not all that dependent on the nucleophile, with changes in energy for most of the substituted chlorinated methanes being quite small relative to the nonsubstituted chlorinated methanes. Relative to the nonsubstituted chlorinated methanes, the $CH_xCl_{3-x}F$ and $CH_xCl_{3-x}OH$ compounds are moderately more difficult to reduce, the $CH_xCl_{3-x}SH$ compounds are moderately less difficult to reduce, and the $CH_xCl_{3-x}(HCO_3)$

TABLE 5: One-Electron Gas-Phase Enthalpies of Reactions (kcal/mol)

compounds	pathway 1	pathway 2	pathway 3	pathway 4
CCl_4	−12.9		23.9	
$CHCl_3$	−7.8		44.4	
CH_2Cl_2	−5.4		64.3	
CH_3Cl	−1.8		83.9	
CCl_3SH	−13.2	12.4	29.4	16.9
$CHCl_2SH$	−9.2	15.6	53.2	35.5
CH_2ClSH	−8.8	16.0	63.2	53.5
$CCl_3(HCO_3)$	−10.0	−5.8	27.3	39.5[b]
$CHCl_2(HCO_3)$	−3.2	2.6	46.8	63.3[b]
$CH_2Cl(HCO_3)$	−2.5	3.2	67.1	81.5[b]
CCl_3OH	−7.1	53.5	35.2	49.0
$CHCl_2OH$	−4.4	53.2	59.7	64.0
CH_2ClOH	−5.0	49.0	84.5	77.4
CCl_3F	−8.7	26.0	28.7	58.2
$CHCl_2F$	−3.9	29.8	55.2	77.4
CH_2ClF	−0.9	29.6	80.0	94.7
$CCl_3(NO_3)$	−60.9[a]	−15.4	[c]	26.9
$CHCl_2(NO_3)$	−54.4[a]	−11.4	[c]	46.3
$CH_2Cl(NO_3)$	−43.3[a]	−12.7	[c]	62.6

[a] Enthalpy of reaction for eq 5. [b] $\Delta H_f^\circ(HCO_3) = -81.5$ kcal/mol and $S^\circ(HCO_3) = 65.30$ cal mol^{-1} K^{-1} values used in calculation. $\Delta H_f^\circ(HCO_3)$ obtained from isodesmic reaction $HCO_2 + CH_3OH \rightarrow HCO_3 + CH_4$ at the MP2/cc-pVDZ level, and $S^\circ(HCO_3)$ obtained at the MP2/cc-pVDZ level. [c] Cannot be estimated because $\Delta H_f^\circ(CH_xCl_{2-x}(NO_3)^-)$ could not be calculated due to dissociation of the complex.

TABLE 6: One-Electron Aqueous-Phase Free Energies of Reactions (kcal/mol)

compounds	pathway 1	pathway 2	pathway 3	pathway 4
CCl_4	−58.2		1.7	
$CHCl_3$	−54.3		17.8	
CH_2Cl_2	−51.0		27.4	
CH_3Cl	−45.3		32.3	
CCl_3SH	−61.1	−33.0	4.5	−7.1
$CHCl_2SH$	−56.7	−29.2	19.1	8.5
CH_2ClSH	−53.8	−27.5	28.7	16.9
$CCl_3(HCO_3)$	−57.8	−48.9	4.9	6.1[b]
$CHCl_2(HCO_3)$	−53.9	−43.8	20.3	23.0[b]
$CH_2Cl(HCO_3)$	−46.9	−38.3	39.6	35.1[b]
CCl_3OH	−54.8	−19.2	8.8	24.0
$CHCl_2OH$	−50.7	−17.5	29.5	37.5
CH_2ClOH	−48.4	−21.6	41.6	40.0
CCl_3F	−55.3	−48.9	3.4	35.7
$CHCl_2F$	−51.6	−45.4	23.4	51.0
CH_2ClF	−47.6	−45.7	34.3	57.4
$CCl_3(NO_3)$	−118.4[a]	−54.9	[c]	−10.1
$CHCl_2(NO_3)$	−109.7[a]	−48.0	[c]	8.6
$CH_2Cl(NO_3)$	−96.5[a]	−48.1	[c]	15.2

[a] Solution-phase free energy of reaction for eq 5. [b] $\Delta H_f^\circ(HCO_3) = -81.5$ kcal/mol and $S^\circ(HCO_3) = 65.30$ cal mol^{-1} K^{-1} values used in calculation. $\Delta H_f^\circ(HCO_3)$ obtained from isodesmic reaction $HCO_2 + CH_3OH \rightarrow HCO_3 + CH_4$ at the MP2/cc-pVDZ level, and $S^\circ(HCO_3)$ obtained at the MP2/cc-pVDZ level. [c] Cannot be estimated because $\Delta H_f^\circ(CH_xCl_{2-x}(NO_3)^-)$ could not be calculated due to the dissociation of the complex.

SCHEME 1

$$\begin{tikzcd}
\mathrm{CH_xCl_{3-x}}L_{(g)} \arrow[d, "\Delta G_s^a"] & +\ 1e^-_{(g)} \arrow[d, "\Delta G_s^b"] & \rightarrow\ \mathrm{CH_xCl_{2-x}}L^\bullet_{(g)} \arrow[d, "\Delta G_s^c"] & +\ \mathrm{Cl}^-_{(g)} \arrow[d, "\Delta G_s^d"] \\
\mathrm{CH_xCl_{3-x}}L_{(aq)} & +\ 1e^-_{(aq)} & \rightarrow\ \mathrm{CH_xCl_{2-x}}L^\bullet_{(aq)} & +\ \mathrm{Cl}^-_{(aq)}
\end{tikzcd}$$

$$\Delta G_{rxn}^{solv} = \left(\Delta G_s^c - \Delta G_s^a\right) + \left(\Delta G_s^d - \Delta G_s^b\right) \approx \left(\Delta G_s^c - \Delta G_s^a\right) - 38 kcal/mol$$

compounds are comparable. However, the nitrate-substituted compounds, $CH_xCl_{3-x}(NO_3)$, exhibit more dramatic changes in energy. Contrary to the small gains in energy observed for most of the substituted compounds, the nitrate-substituted compounds gain a substantial amount of energy during reduction. This significant gain in energy supports the rudimentary oxidation−reduction argument that a nitrogen atom in a formal +5 oxidation state will more readily reduce than a carbon atom in the formal oxidation state of +4, +2, or −2. We note that the nitrate combinations lead to the loss of Cl^- and NO_2.

In addition, Table 5 shows that the reduction of the compounds considered in this study are strongly dependent on the degree of chlorination. Compounds with 3 chlorine atoms are, on average, 8 kcal/mol easier to reduce than compounds with only a single chlorine. In the simplest model, the highly polar C−Cl bonds should strengthen the bonding network around the carbon center. However, as pointed out by Kumaran et al., chlorine substitutions appear to have an almost exclusively steric effect[71] and, in fact, the C−Cl bonds get weaker as the number of chlorines increases. In contrast, increased fluorination increases the C−F bond strength.[29] This steric effect causes the other bonds present in the $CH_xCl_{3-x}L$ compounds to weaken. A similar steric effect is consistent with the results seen for the $CH_xCl_{3-x}SH$ compounds, whereas for the $CH_xCl_{3-x}F$, $CH_xCl_{3-x}OH$, and $CH_xCl_{3-x}(HCO_3)$ compounds polar factors seem to be more important.

The aqueous-phase reaction free energies are given in Table 6 and allow us to investigate the role of solvation. Table 6 was generated by using experimental and high quality ab initio values for $\Delta G_f^\circ(e^-(aq))$, $\Delta G_f^\circ(L^-(aq))$, $\Delta G_f^\circ(Cl^-(aq))$, $\Delta G_f^\circ(L^\bullet(g))$, $\Delta G_f^\circ(Cl^\bullet(g))$, $\Delta G_f^\circ(CH_xCl_{4-x}(aq))$, $\Delta G_f^\circ(CH_xCl_{3-x}L(aq))$, $\Delta H_f^\circ(Cl_2CO(g))$, and $\Delta H_f^\circ(H_2CO(g))$ found in Tables A1 and A2 (see Appendix) and the remaining values, $\Delta H_f^\circ(CH_xCl_{2-x}L^\bullet(g))$, $\Delta H_f^\circ(CH_xCl_{2-x}L^-(g))$, $\Delta H_f^\circ(HClCO(g))$, $S^\circ(Cl_2CO(g))$, $S^\circ(HClCO(g))$, $S^\circ(H_2CO(g))$, $S^\circ(CH_xCl_{2-x}L^\bullet(g))$, $S^\circ(CH_xCl_{2-x}L^-(g))$, $S^\circ(HClCO(g))$, $\Delta G_s(L^\bullet)$, $\Delta G_s(Cl^\bullet)$, $\Delta G_s(CH_xCl_{2-x}L^\bullet)$, $\Delta G_s(CH_xCl_{2-x}L^-)$, $\Delta G_s(Cl_2CO)$, $\Delta G_s(HClCO)$, $\Delta G_s(H_2CO)$, and $\Delta G_s(CH_xCl_{2-x}L^-)$, were obtained from Tables 1, 2, and 4 at the MP2/cc-pVDZ and MP2/aug-cc-pVDZ levels. For the lowest energy pathway (pathway 1) the influence of solvation on relative energetics between the different substituted chlorinated methanes is negligible. In most cases, the relative energetics of pathway 1 changes by only a few kcal/mol upon solvation. The reduction of nitrate-substituted compounds via pathway 1 is slightly more affected by solvation, where the reduction of the nitrate-substituted species relative to the nonsubstituted species is seen to be ∼10 kcal/mol more favorable in solution then in the gas phase. The small changes in relative energies for pathway 1 can be easily understood by tracing the free energy changes, ΔG_{rxn}^{solv}, associated with solvation for pathway 1 (Scheme 1).

In this scheme, the majority of solvation energy comes from the difference of the heat of solution of the chloride and the electron ($\Delta G_s^b \approx 1.6$ eV,[64] $\Delta G_s^d \approx -75$ kcal/mol, $(\Delta G_s^d - \Delta G_s^b) \approx -38$ kcal/mol), where ΔG_s^d was estimated by using eq 16b with $\Delta G_f^\circ(Cl^-(aq)) = -31.36$ kcal/mol,[118] $\Delta H_f^\circ(Cl^-(g)) = -55.92$ kcal/mol,[20] and $S^\circ(Cl^-(g)) = 36.654$ cal mol^{-1} K^{-1} [20]). The differences in solvation energy for the $CH_xCl_{2-x}L^\bullet$ and $CH_xCl_{3-x}L$ compounds are less than a kcal/mol in most cases. For the next lowest energy pathway (pathway 2) the effect of the solvent is somewhat correlated to the size of anion with respect to the size of the Cl^- anion. Comparing Tables 5 and 6, we see that the reactions where the less bulky anions, i.e., F^- and OH^-, are being expelled are substantially more exothermic as compared to the gas-phase value when the effects of solvent are included. The most dramatic improvements are seen for the reduction of CH_2ClF where the difference between pathways 1 and 2 is only 2 kcal/mol in solution, compared to 30 kcal/mol

TABLE A1: Experimental and High-Quality ab Initio Gas-Phase Enthalpies of Formation (kcal/mol) Used in Computations

compd	ΔH_f°	compd	ΔH_f°	compd	ΔH_f°
H_2	0	CCl_4	−24.59[c]	$CCl_3(HCO_3)$	−150.79[f]
e^-	0.00[c]	CCl_3H	−24.65[c]	$CHCl_2(HCO_3)$	−154.11[f]
$H^\bullet$	52.10[c]	CCl_2H_2	−22.10[c]	$CH_2Cl(HCO_3)$	−149.82[f]
$C^\bullet$	171.29[c]	$CClH_3$	−19.32[c]	$CH_3(HCO_3)$	−145.10[d]
$N^\bullet$	112.98[c]	CH_4	−17.88[c]	CCl_3F	−69.00[b]
$O^\bullet$	59.55[c]	CCl_3OH	−69.43[f]	$CHCl_2F$	−67.70[b]
$F^\bullet$	18.97[b]	$CHCl_2OH$	−63.97[f]	CH_2ClF	−62.60[b]
$S^\bullet$	66.64[c]	CH_2ClOH	−54.96[f]	CH_3F	−56.00[b]
$Cl^\bullet$	29.08[c]	CH_3OH	−47.96[c]	$CCl_3^\bullet$	19.00[b]
$NO_2^\bullet$	7.911[b]	CCl_3SH	−13.40[f]	CCl_3^-	−33.1[h]
$OH^\bullet$	9.319[b]	$CHCl_2SH$	−11.48[f]	$CH_3^\bullet$	34.82[b]
$SH^\bullet$	33.30[b]	CH_2ClSH	−7.01[f]	CH_3^-	33.2[b]
$NO_3^\bullet$	17.00[b]	CH_3SH	−5.34[c]	Cl_3CO^-	−120.9[i]
Cl^-	−55.92[b]	$CCl_3(NO_3)$	−39.71[f]	CH_3O^-	−32.2[g]
OH^-	−34.32[b]	$CHCl_2(NO_3)$	−38.63[f]	Cl_2CO	−52.60[b]
SH^-	−19.4[b]	$CH_2Cl(NO_3)$	−32.42[f]	H_2CO	−27.70[b]
NO_3^-	−73.48[b]	$CH_3(NO_3)$	−29.80[c]	H_2CS	−28.3
HCO_3^-	−175.0[a]			H_2O	−57.80[b]
F^-	−61.4[b,e]			$HCO_2^\bullet$	−28.2[j]

[a] Calculated at the G2(MP2) level from the acidity of the parent.[19] [b] Experimental reference.[20] [c] Experimental reference.[118] [d] Experimental reference.[54] [e] $H_f^\circ(298.15\ K)$ calculated from $\Delta H_f^\circ(0\ K)$ + ideal gas correction. [f] Values obtained from isodesmic calculations at the MP2/cc-pVDZ level.[19] [g] Experimental reference.[2,99] [h] Experimental reference.[2,88] [i] Value based on $\Delta H_f^\circ(298.15\ K)$ of Cl^- and Cl_2CO, and the experimental chloride affinity of Cl_2CO (12.4 kcal/mol) from ref 73. [j] CCSD(T) calculation extrapolated to the complete basis set limit based on aug-cc-pVDZ, T, Q with ZPE, core-val, and relativistic corrections.[40]

TABLE A2: Experimental and High-Quality ab Initio Aqueous-Phase Free Energies of Formation (kcal/mol) Used in Computations

compd	ΔG_f°	compd	ΔG_f°	compd	ΔG_f°
e^-	64.80[a,b]	CCl_4	−11.25[c,f]	$CCl_3(HCO_3)$	−129.49[d,j]
$Cl^\bullet$	28.42[c,e]	CCl_3H	−14.95[c,f]	$CHCl_2(HCO_3)$	−133.96[d,j]
$OH^\bullet$	5.42[d,e]	CCl_2H_2	−14.43[c,f]	$CH_2Cl(HCO_3)$	−136.00[d,j]
$SH^\bullet$	28.58[d,e]	$CClH_3$	−12.06[c,f]	CCl_3F	−55.81[d,g]
$NO_3^\bullet$	18.63[d,e]	CCl_3OH	−56.60[d,j]	$CHCl_2F$	−58.73[d,h]
$NO_2^\bullet$	14.02[d,e]	$CHCl_2OH$	−57.64[d,j]	CH_2ClF	−55.08[d,h]
$F^\bullet$	17.82[d,e]	CH_2ClOH	−50.08[d,j]	Cl_2CO	−45.48[d,e]
Cl^-	−31.36[i]	CCl_3SH	−2.25[d,j]	$HClCO$	−43.05[j,e]
OH^-	−37.58[i]	$CHCl_2SH$	−5.44[d,j]	H_2CO	−26.34[d,e]
SH^-	2.89[i]	CH_2ClSH	−3.74[d,j]		
NO_3^-	−25.99[i]	$CCl_3(NO_3)$	−9.20[d,j]		
HCO_3^-	−140.24[i]	$CHCl_2(NO_3)$	−15.51[d,j]		
F^-	−66.63[i]	$CH_2Cl(NO_3)$	−12.01[d,j]		

[a] $\Delta G_s(e^-) = 1.6$ eV from ref 64. [b] $E_H^\circ = 101.7$ from eq 23. [c] ΔG_f° obtained from experimental reference.[118] [d] ΔG_f° obtained from experimental reference.[20] [e] ΔG_s obtained from SCRF calculations at the MP2/cc-pVDZ level. [f] ΔG_s obtained from experimental reference.[84] [g] ΔG_s obtained from experimental reference.[106] [h] ΔG_s obtained from experimental reference.[124] [i] $\Delta G_f^\circ(aq)$ obtained from experimental reference.[118] [j] ΔG_f° obtained from isodesmic and entropy calculations at the MP2/cc-pVDZ level (this work and ref 19).

in the gas phase. In contrast, the reactions with the bulkier anions, i.e., SH^-, NO_3^-, and HCO_3^- are only slightly more exothermic than the gas-phase values when the effects of solvent are included. Finally, the higher energy pathways 3 and 4 are still predicted to be very unlikely pathways when the effects of solvent are included.

TABLE A3: Standard States for Entropies (cal mol^{-1} K^{-1})

atomic standard states	
$^1/_2H_2$	15.617[a]
C, graphite	1.372[a]
$^1/_2N_2$	22.898[a]
$^1/_2O_2$	24.515[a]
$P_{(s)}$, white	9.821[a]
$S_{(s)}$	7.600[a]
$^1/_2Cl_2$	27.845[a]
$^1/_2F_2$	24.221[a]

[a] Experimental reference.[118]

VII. Conclusion

Ab initio electronic structure theory, canonical ensemble entropy formulas, and self-consistent reaction field theory were used to estimate the thermochemical properties, $\Delta H_f^\circ(298.15\ K)$, $S^\circ(298.15\ K, 1\ bar)$, and $\Delta G_S(298.15\ K, 1\ bar)$, for the substituted chloromethyl radicals and anions: $CCl_3^\bullet$, $CHCl_2^\bullet$, $CH_2Cl^\bullet$, $CCl_2F^\bullet$, $CHClF^\bullet$, $CH_2F^\bullet$, $CCl_2OH^\bullet$, $CHClOH^\bullet$, $CH_2OH^\bullet$, $CCl_2SH^\bullet$, $CHClSH^\bullet$, $CH_2SH^\bullet$, $CCl_2(HCO_3)^\bullet$, $CHCl(HCO_3)^\bullet$, $CH_2(HCO_3)^\bullet$, CCl_3^-, $CHCl_2^-$, CH_2Cl^-, CCl_2F^-, $CHClF^-$, CH_2F^-, CCl_2OH^-, $CHClOH^-$, CH_2OH^-, CCl_2SH^-, $CHClSH^-$, CH_2SH^-, $CCl_2(HCO_3)^-$, $CHCl(HCO_3)^-$, and $CH_2(HCO_3)^-$. In addition, thermochemical properties were used to estimate $\Delta H_f^\circ(298.15\ K)$, $S^\circ(298.15\ K, 1\ bar)$, and $\Delta G_S(298.15\ K, 1\ bar)$ for the aldehyde ClHCO, and the *gem*-chlorohydrin anions CCl_3O^-, $CHCl_2O^-$, and CH_2ClO^-. These additional compounds were estimated because the $CH_xCl_{2-x}(NO_3)^\bullet$ and $CH_xCl_{2-x}(NO_3)^-$ compounds were not stable, with all levels of ab initio theory producing dissociating complexes. The most difficult computational step in our thermodynamic estimations was determining the gas-phase enthalpies of formation, $\Delta H_f^\circ(298.15\ K)$. For this, a strategy based on isodesmic hydrogen exchange reactions was used to reduce the error associated with determining $\Delta H_f^\circ(298.15\ K)$. This strategy, at the MP2 level of theory, was found be quite reliable (within 2 kcal/mol) for determining the gas-phase enthalpies of formation for the substituted methyl radicals and methyl anions. Furthermore, this strategy was found to be reasonably accurate even when lower level ab initio methods were used. Our results did not suggest a best lower level ab initio method for the entire set of compounds studied. However, the B3LYP/DZVP2 results seemed the most reliable for the substituted methyl radicals, whereas LDA/aug-DZVP2 results seem to work the best for the substituted methyl anions.

The calculated thermochemical properties allowed us to estimate the energetics of several one-electron reductive pathways. By using these data, we calculated the thermodynamics of reducing substituted chlorinated methanes via the commonly accepted pathway to a substituted chlorinated methyl radical and a chloride. In addition, we also estimated one-electron reduction pathways involving the production of carbanions and pathways involving the loss of other anions. Our results agree with the available experimental data, which show that the only thermodynamically accessible pathway in most cases was the accepted pathway, forming a substituted chlorinated methyl radical and a chloride. The exception was for the nitrate-substituted compounds. In this case the one-electron reduction pathway was predicted to follow a novel one-electron reduction pathway, forming an aldehyde, Cl^- anion, and NO_2 gas.

In summary, our thermodynamic results showed, relative to the nonsubstituted chlorinated methanes, that the $CH_xCl_{3-x}F$ and $CH_xCl_{3-x}OH$ compounds are moderately more difficult to reduce, the $CH_xCl_{3-x}SH$ compounds are moderately less difficult to reduce, the $CH_xCl_{3-x}(HCO_3)$ compounds are comparable to reduce, and the $CH_xCl_{3-x}(NO_3)$ compounds are substantially easier to reduce. In addition, the results of this study suggest that a higher degree of chlorination correspond to a more favorable reduction. This trend, previously explained by Kumaran et al,[71] is the result of Cl substitutions having an almost exclusively steric effect. Finally, the results of this study demonstrate that ab initio electronic structure methods can be used to calculate the reaction energetics of a potentially large number of organic compounds in solution, including radical and anionic compounds for which experimental data are unavailable, and can be used to help identify the potentially important environmental degradation reactions.

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Supporting Information Available: Tables of ab initio total energies, and enthalpy corrections for gas-phase $CH_xCl_{3-x}L$, $CH_xCl_{2-x}L^\bullet$ and $CH_xCl_{2-x}L^-$ compounds determined from LDA/DZVP2, LDA/aug-DZVP2, BP91/DZVP2, BP91/aug-DZVP2, B3LYP/DZVP2, B3LYP/aug-DZVP2, MP2/cc-pVDZ, and MP2/aug-cc-pVDZ total energy and vibrational calculations. Also, a table of exponents for the aug-DZVP2 diffuse functions determined from an even-tempered strategy is specified. In addition to the Supporting Information available, the optimized structures for all the molecules calculated can be obtained by correspondence with E.J.B. (Eric.Bylaska@pnl.gov) or D.A.D. (David.Dixon@pnl.gov).

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