The Free Energies of Reactions of Chlorinated Methanes with Aqueous Monovalent Anions: Application of Ab Initio Electronic Structure Theory

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The presence of different anionic species in natural waters can significantly alter the degradation rates of chlorinated methanes and other organic compounds. Favorable reaction energetics is a necessary feature of these nucleophilic substitution reactions that can result in the degradation of the chlorinated methanes. In this study, ab initio electronic structure theory is used to evaluate the free energies of reaction of a series of monovalent anionic species (OH^-, SH^-, NO_3^-, HCO_3^-, HSO_3^-, HSO_4^-, $H_2PO_4^-$, and F^-) that can occur in natural waters with the chlorinated methanes, CCl_4, CCl_3H, CCl_2H_2, and $CClH_3$. The results of this investigation show that nucleophilic substitution reactions of OH^-, SH^-, HCO_3^-, and F^- are significantly exothermic for chlorine displacement, NO_3^- reactions are slightly exothermic to thermoneutral, HSO_3^- reactions are slightly endothermic to thermoneutral and HSO_4^-, and $H_2PO_4^-$ reactions are significantly endothermic. In the case of OH^-, SH^-, and F^- where there are limited experimental data, these results agree well with experiment. The results for HCO_3^- are potentially important given the near ubiquitous occurrence of carbonate species in natural waters. The calculations reveal that the degree of chlorination, with the exception of substitution of OH^-, does not have a large effect on the Gibbs free energies of the substitution reactions. These results demonstrate that ab initio electronic structure methods can be used to calculate the reaction energetics of a potentially large number of organic compounds with other aqueous species in natural waters and can be used to help identify the potentially important environmental degradation reactions.

I. Introduction

In natural waters, chlorinated hydrocarbons (CHCs) from anthropogenic sources (as well as natural ones) come in contact with a variety of anions, which through nucleophilic substitution reactions can cause degradation by substituting for a Cl^-.[1−4] Despite their potential to have a significant influence on the degradation of CHCs, reactions between many environmentally important anions and CHCs are still not well understood. In addition, they also have the potential to form compounds that are even more persistent and hazardous than the parent CHCs.[5,6]

It has long been known that OH^- can significantly increase the reactivity of CHCs,[7] and in recent times the importance of SH^- has been demonstrated in both laboratory and field investigations.[5,8] Rarely, however, are anionic species other than OH^- considered in models that attempt to discern possible degradation pathways for CHCs found in natural waters. There are two compelling reasons as to why other anions may play an important role in the environmental degradation of CHCs. The first is that monochlorinated hydrocarbons are known to undergo substitution reactions with many kinds of nucleophiles.[9−11] The second is that significant amounts of unidentified nonvolatile compounds have been found in many laboratory experiments of the degradation of CHCs in aqueous systems.[12−15]

In this work, we report a quantitative ab initio electronic structure study of the reaction energies of anionic nucleophilic substitution reactions between chlorinated methanes and environmentally important anions. Our focus here is on obtaining accurate predictions of the enthalpies and free energies of reaction. Of course, favorable thermodynamics is a necessary, albeit not complete, condition for these substitution reactions to proceed under ambient conditions. In this work we combine a variety of theoretical methods, starting from ab initio electronic structure calculations and then using isodesmic reaction schemes, gas-phase entropy estimates, and continuum solvation models to provide estimates of the free energies for the following reactions:

$$N^-_{(aq)} + CCl_{4(aq)} \rightarrow CCl_3N_{(aq)} + Cl^-_{(aq)}$$

$$N^-_{(aq)} + CCl_3H_{(aq)} \rightarrow CCl_2HN_{(aq)} + Cl^-_{(aq)}$$

$$N^-_{(aq)} + CCl_2H_{2(aq)} \rightarrow CClH_2N_{(aq)} + Cl^-_{(aq)}$$

$$N^-_{(aq)} + CClH_{3(aq)} \rightarrow CH_3N_{(aq)} + Cl^-_{(aq)}$$

where $N^- = OH^-$, SH^-, NO_3^-, HCO_3^-, HSO_3^-, HSO_4^-, $H_2PO_4^-$, F^-.

Our objective is not only to elucidate the specific reaction energies but also to develop computational approaches that we can use to study a wider variety of chlorinated hydrocarbons as well as reaction kinetics. Future work will focus on detailed mechanisms and barriers for reactions that we find to be thermodynamically favorable.

The development of a computational scheme that can accurately predict the above reaction energies requires some care. Even though ab initio electronic structure methods are constantly being developed and improved upon, these methods are rarely able to give heat of formations of a broad class of molecules with error limits of less than a few kcal/mol.[16−18] Only when very large basis sets such as the correlation-consistent basis sets,[19−24] high level treatments of correlation energy such as coupled cluster methods (CCSD(T)),[25−27] and small correction factors such as core−valence correlation energies and relativistic effects are included will the heat of formation from ab initio electronic structure methods be accurate to within 1 kcal/mol.[28−36] Although one can now accurately calculate the heats of formation of molecules with up to six

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first row atoms, such high-level calculations are extremely demanding and scale computationally as N^7 for N basis functions. In addition to issues associated with ab initio electronic structure methods, our objective here, which is the determination of free energies of reaction in solution, also requires that solvation and entropic contributions be included in addition to changes in enthalpy.

In this paper, we address these difficulties by using separate computational steps to deal with the issues of electronic energy differences, entropy, and solvation. First, the enthalpies of formation of gas-phase $CH_xCl_{y-1}N$ species are calculated followed by the calculation of entropies of gas-phase $CH_xCl_{y-1}N$ species. These combined calculations yield the free energy of gas-phase $CH_xCl_{y-1}N$ species. Finally, the solvation energies of CH_xCl_y and $CH_xCl_{y-1}N$ species are calculated. The solvation calculations account for the effect of solvent on gas-phase energetics. In such calculations, the basic assumption is that bonding relations within the $CH_xCl_{y-1}N$ species do not change substantially when going from the gas phase to the solution phase. The desired results of this work, reaction energies in both the gas phase and solution phase, can now be estimated, because the necessary thermodynamic quantities are known either from experiment or obtained from the calculations described herein.

In section II, the computational methods used in this work are described. The results of the calculations of the enthalpies of formation of gas-phase $CH_xCl_{y-1}N$ species are reported in section III. The difficulties associated with calculating absolute heats of formation from atomization energies are avoided by using a set of isodesmic reactions. The isodesmic reactions (i.e., the same number of chemical bond types for products and reactants) are used to relate the unknown enthalpies of formation of gas-phase $CH_xCl_{y-1}N$ species to the known experimental enthalpies of formation of gas-phase CH_xCl_y and CH_3N species. The choice of this method is based on results from many studies,[37] which show that using isodesmic reactions leads to excellent agreement with experiment. Section IV reports the calculations of the entropies of the gas-phase $CH_xCl_{y-1}N$ species using standard statistical mechanical expressions for the vibrational, rotational, and translational entropy contributions. Section V reports the calculations of the solvation energies of the $CH_xCl_{y-1}N$ and CH_xCl_y species using the continuum solvation model of Tomasi et al.[38,39] Such a treatment of solvation is more computationally efficient than explicitly doing simulations with water molecules, and it has been shown[40] to give solvation energies within a few kcal/mol, which for this study is adequate considering the errors in the gas-phase enthalpies of formation. Section VI assembles the results to provide estimates of the reaction energetics of the chlorinated methanes CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl interacting with monovalent anionic nucleophiles, and concluding remarks are given in section VII.

II. Ab Initio Calculations

All of the calculations performed in this study were done with the *Gaussian-94*,[41] *Gaussian-98*,[42] or NWChem[43] program systems. Most of the calculations performed in this study were done at the density functional theory (DFT)[44] level and at the second-order Moller−Plesset perturbation theory (MP2) level.[45] The Kohn−Sham equations[46] of DFT were solved using the LDA,[47] BP91,[48,49] and B3LYP[50,51] exchange-correlation functionals with the polarized double-ζ DZVP2[52] basis set. The MP2 calculations were done using the correlation-consistent cc-VDZ[19−24] basis set. Certain calculations performed in this study required higher accuracy and were done either at the G2[17] or G2(MP2)[53] levels. The G2 level is slightly more accurate than the G2(MP2) level, but the latter is computationally more efficient. However, the accuracy of both of these levels is quite good, and both have reproduced experimental atomization energies to within a few kcal/mol for many molecules.

TABLE 1: Ab Initio Values of Standard Enthalpy of Formation (ΔH°_f(298 K)) for CCl_3F Species Calculated Using the Atomization Approach[a]

	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2	G2	exp.
ΔH°_f	−41.01	−79.11	−59.73	−37.57	−72.50	−69.00[b]

[a] All quantities are in kcal/mol. [b] Experimental ref 55.

Solvent effects were estimated by using the self-consistent reaction field (SCRF) theory of Tomasi et al.[38−40,54] This continuum model can be used with a variety of ab initio electronic structure levels. In this study, SCRF calculations were done at the LDA/DZVP2, BP91/DZVP2, B3LYP/DZVP2, and MP2/cc-pVDZ levels.

III. Calculation of Gas-Phase Enthalpies of Formation

The enthalpies of formation for the gas-phase CCl_3N, CCl_2HN, $CClH_2N$, and CH_3N species have been calculated as follows. Two approaches were used to perform these calculations, one for calculating enthalpies of formation for CCl_3N, CCl_2HN, and $CClH_2N$ species, and another for calculating CH_3N species whose experimental values were not available. The enthalpies of formation for the CCl_3N, CCl_2HN, and $CClH_2N$ species were calculated using an isodesmic scheme.[37] This scheme should provide accurate heats of formation, within a few kcal/mol, and is computationally tractable. However, the enthalpies of formations for CH_4, $CClH_3$, CCl_2H_2, CCl_3H, and CH_3N species must be known. Fortunately, most of these enthalpies of formation are available from experiment, except for the $CH_3(HSO_3)$, $CH_3(HSO_4)$, and $CH_3(H_2PO_4)$ molecules. The enthalpies of formation for these three molecules were calculated using the second scheme based on atomization energies calculated at the G2 level. The G2 method calculates the atomization energies based on an additivity correction scheme. Unfortunately, unlike the isodesmic approach, the G2 approach is significantly more expensive as a QCISD(T) calculation is needed.

Even at the G2 level, it is not always possible to calculate the heat of formation to within ±1 kcal/mol, and other methods can have even more difficulty. For example, the G2 value for $\Delta H_f(CF_4)$ at 0 K is −227.2 kcal/mol[18] as compared to the JANAF value of −221.6 ± 0.3 kcal/mol,[55] an error of 5.6 kcal/mol. Similarly, the G2 value for $\Delta H_f(C_2F_4)$ at 0 K is −164.8 kcal/mol,[18] compared to the experimental value of −156.6 ± 0.7 kcal/mol,[55] an error of 8.2 kcal/mol. It is useful to note that the G2 values are more negative (higher atomization energy) than the experimental ones. However, the G2 method is significantly better than many other methods for calculating heats of formation based on atomization energies. We provide a specific example for CCl_3F as shown in Table 1. The enthalpy of formation for CCl_3F is calculated by using atomization energies from different levels of ab initio theory and errors of up to 30 kcal/mol are found. This example demonstrates that care must be taken in choosing the appropriate method for calculating heats of formation from total atomization energies.

The calculated enthalpies of reaction for the following isodesmic reactions:

$$CCl_3N + CH_4 \rightarrow CH_3N + CCl_3H$$

$$CCl_2HN + CH_4 \rightarrow CH_3N + CCl_2H_2$$

$$CClH_2N + CH_4 \rightarrow CH_3N + CClH_3$$

TABLE 2: Gas-Phase Standard Enthalpies of Formation (ΔH°_f(298 K)) from Isodesmic Reactions and G2[a]

	ΔH°_f(298.15 K) (isodesmic formulation)				ΔH°_f(298.15 K)	
	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2	G2	exp
CCl_3OH	−69.43	−69.21	−65.15	−64.01	−68.35	
$CHCl_2OH$	−63.97	−64.36	−62.60	−61.62	−64.16	
CH_2ClOH	−54.96	−54.87	−54.09	−53.70	−59.79	
CH_3OH					−49.26	−47.96[e]
CCl_3SH	−13.40	−11.86	−8.68	−7.64	−12.95	
$CHCl_2SH$	−11.48	−11.07	−8.66	−7.92	−11.52	
CH_2ClSH	−7.01	−6.66	−5.44	−5.20	−6.98	
CH_3SH					−4.76	−5.34[e]
$CCl_3(NO_3)$	−39.71	−35.04	−32.83	−29.12	−38.61	
$CHCl_2(NO_3)$	−38.63	−36.78	−34.90	−32.60		
$CH_2Cl(NO_3)$	−32.42	−31.85	−30.71	−29.87		
$CH_3(NO_3)$					−32.39	−29.80[e]
$CCl_3(HCO_3)$	−150.79	−149.97	−145.53	−144.09		
$CHCl_2(HCO_3)$	−154.11	−153.70	−150.73	−149.45		
$CH_2Cl(HCO_3)$	−149.82	−150.33	−148.53	−147.59		
$CH_3(HCO_3)$					−144.61	−145.1[d]
$CCl_3(HSO_3)$[b]	−129.54	−126.54	−124.50	−121.75		
$CHCl_2(HSO_3)$[b]	−128.87	−129.04	−124.65	−122.84		
$CH_2Cl(HSO_3)$[b]	−122.78	−122.88	−121.54	−120.22		
$CH_3(HSO_3)$[b]					−115.57	
$CCl_3(HSO_4)$[b]	−165.73	−168.78	−166.56	−164.36		
$CHCl_2(HSO_4)$[b]	−164.75	−169.18	−163.89	−165.90		
$CH_2Cl(HSO_4)$[b]	−163.85	−169.53	−169.13	−168.41		
$CH_3(HSO_4)$[b]					−162.31	
$CCl_3(H_2PO_4)$[b]	−271.88	−270.30	−265.62	−263.88		
$CHCl_2(H_2PO_4)$[b]	−272.77	−272.77	−268.62	−267.33		
$CH_2Cl(H_2PO_4)$[b]	−268.55	−269.50	−266.48	−265.51		
$CH_3(H_2PO_4)$[b]					−260.57	
CCl_3F	−71.51	−72.35	−68.57	−67.10	−72.50	−69.00[c]
CCl_2HF	−68.88	−70.15	−67.10	−65.76		−67.70[c]
$CClH_2F$	−63.29	−64.36	−62.61	−61.72	−65.11	−62.60[c]
CH_3F					−58.23	−56.00[c]

[a] Experimental and ab inito total energy values used to determine these enthalpies of formations are given in Tables 3 and 7 and as Supporting Information. All quantities are in kcal/mol. The isodesmic exchange reactions are: $CCl_xH_yN + CH_4 \rightarrow Cl_xH_{y+1} + CH_3N$. [b] G2 theoretical values were used for the enthalpies of formation of $CH_3(HSO_3)$, $CH_3(HSO_4)$, and $CH_3(H_2PO_4)$. See text. [c] Experimental reference 55. [d] Experimental reference 66. [e] Experimental reference 67.

TABLE 3: Miscellaneous Experimental and G2(MP2) Gas-Phase Enthalpies of Formation (kcal/mol)

compd	ΔH°_f	compd	ΔH°_f	compd	ΔH°_f
H	52.095[c]	CCl_4	−24.59[c]	Cl^-	−55.92[b]
C	171.291[c]	CCl_3H	−24.65[c]	OH^-	−34.32[b]
N	112.979[c]	CCl_2H_2	−22.10[c]	SH^-	−19.4[b]
O	59.553[c]	$CClH_3$	−19.32[c]	NO_3^-	−73.48[b]
F	18.974[b]	CH_4	−17.88[c]	HCO_3^-	−175.0[a]
P	75.201[c]			HSO_3^-	−166.5[a]
S	66.636[c]			HSO_4^-	−231.2[b]
Cl	29.082[c]			$H_2PO_4^-$	−309.2[a]
				F^-	−61.4[b,d]

[a] Calculated at the G2(MP2) level from the acidity of the parent. [b] Experimental reference 55. [c] Experimental reference 67. [d] ΔH°_f(298.15 K) calculated from ΔH°_f(0 K) + ideal gas correction.

were used to determine the enthalpies of formation for the CCl_3N, CCl_2HN, and $CClH_2N$ species. 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 helps to minimize the error in the calculation of the reaction energy. The reaction enthalpy was calculated from the electronic, thermal, and vibrational energy differences at 298.15 K at a consistent level of theory. The enthalpy of formation of the unknown can then be calculated by using Hess's law with the calculated enthalpy change and the known heats of formation of the other three species, which were obtained from experiment or other calculated values. For example, ΔH_f CCl_3N = ΔH_f CH_3N(exp) + ΔH_f CCl_3H(exp) − ΔH_f CH_4(exp) − ΔH_r(calc).

The gas-phase enthalpies of formation for the CCl_3N, CCl_2HN, $CClH_2N$, and CH_3N species reported in Table 2 include calculated values based on the isodesmic approach and at the G2 level for a number of species as well as available experimental values. Other experimental values are given in Table 3. The various ab intio energies needed for the calculations and the isodesmic reaction energies are given as Supporting Information. The first four columns of Table 2 contain values based on the isodesmic reactions at the MP2/cc-pVDZ, LDA/DZVP2, BP91/DZVP2, and B3LYP/DZVP2 levels. 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. The average absolute differences from MP2/cc-pVDZ were 1.42, 3.05, and 4.25 kcal/mol for the LDA/DZVP2, BP91/DZVP2, and B3LYP/DZVP2 methods, respectively. We note that the largest differences from the MP2 values are suprisingly at the B3LYP level. The worst case difference was ~10 kcal/mol and it is between the MP2/cc-pVDZ and B3LYP/DZVP2 calculations for the reaction involving CCl_3NO_3. It is interesting to note that the differences from the MP2 values increase as the number of chlorines increases. Additional insight into the accuracy of the isodesmic scheme can be seen with the fluorinated species, i.e., CCl_3F, $CHCl_2F$, and CH_2ClF species, because their experimental enthalpies of formation are available.[55] In this case, the isodesmic scheme showed a remarkably accurate absolute difference, with differences between the experimental and isodesmic values no worse than 3 kcal/mol. Again, the largest differences are for the most heavily chlorinated compounds. The fifth column of Table 2 contains the G2 values. These calculations were very computationally intensive and so limited the number of calculations of this type that could be done. As previously described, the purpose of these calculations was to provide values for $\Delta H^\circ_f(CH_3(HSO_3))$, $\Delta H^\circ_f(CH_3(HSO_4))$, and $\Delta H^\circ_f(CH_3(H_2PO_4))$. However, to confirm the accuracy of these estimates we calculated the rest of the CH_3N species using G2 theory to allow comparisons with the isodesmic approach and experimental data. The agreement of the G2 values with the experimental ones is reasonable but certainly not within ±1 kcal/mol, with an average absolute difference of 1.9 kcal/mol. Finally, comparisons between the two different schemes (i.e., calculations for the CCl_xH_yOH, CCl_xH_ySH, and $CCl_3(NO_3)$ species) showed that the G2 theory calculations agreed best with the MP2/cc-pVDZ isodesmic calculations, as might be expected considering the importance that MP2 calculations have in the G2 additivity scheme.

We also needed the heats of formation of a number of anions to calculate the gas-phase reaction enthalpies for the various reactions. Table 3 lists the values used in this work. Many of the heats of formation were known from experiment, and the unknown ones were determined using a calculated proton affinity of the anion along with an experimental heat of formation of the neutral protonated anion. We calculated the proton affinity at the G2(MP2) level. For comparison purposes, we calculated the G2(MP2) heat of formation of H_2SO_4, and that of HSO_4^-, from the acidity of H_2SO_4 based on the experimental ΔH_f of H_2SO_4. The G2(MP2) value for ΔH_f (H_2SO_4) is −170.6 kcal/mol as compared to the experimental value of −175.7 ± 2 kcal/mol,[55] a difference of 5 kcal/mol. The calculated value for ΔH_f (HSO_4^-) from the calculated proton affinity and the experimental heat of formation of H_2SO_4 is −231.7 ± 2 kcal/mol as compared to the experimental value of −231.2 ± 2.7 kcal/mol.[56] The heats of formation of HCO_3^-, HSO_3^- and $H_2PO_4^-$ were obtained similarly at the G2(MP2) level and are given in Table 3.

IV. Calculation of the Entropy

Given the structures and vibrational frequencies for a gas-phase molecule, one can calculate its entropy using formulas derived from statistical mechanics.[57,58] In many cases, results from these entropy formulas with accurate structures and frequencies will often provide more accurate values than those determined by direct thermal measurements.

The accuracy of the calculated entropies is lower for molecules with hindered rotations.[59] In these kinds of molecules, e.g., ethane, one of the most important internal degrees of freedom is the rotation of one fragment of a molecule relative to the rest about a single bond connecting the two parts. There are two limiting cases for this kind of rotation. The first is that the barrier impeding the rotation of the functional group is very high; the second is that the rotation about the single bond is essentially unhindered. For highly hindered rotations, the functional group will not rotate except at extremely high temperatures. In this case, the rotation can be considered as a torsional oscillation at ambient temperatures, and thus can be treated as a regular vibration in its contribution to the entropy. However, for temperature ranges where there is nearly free rotation (the second limiting case), one must treat the contribution to the entropy in a different way. To calculate accurate entropies for molecules with nearly unhindered internal bond rotations, we explicitly added a contribution due to each internal bond rotation. Although there were several ways to do this, we chose to use the expressions of Pitzer and Gwinn[59,60] to estimate these contributions. These expressions assume that the bond rotations were unhindered. Despite the simplicity of this approximation, it has been demonstrated that this assumption only slightly overestimates the entropy of a hindered bond rotation.

Table 4 lists experimental and calculated $S°$ at 298.15 K for all the molecules considered in this study. Excellent agreement is seen between the calculated values and the known experimental values. These errors did not exceed 1 cal/mol-K (($T\Delta S$) < 1/2 kcal/mol at $T \sim 300$ K). The CCl_3N, CCl_2HN, $CClH_2N$, and CH_3N species with $N = NO_3$, HCO_3, HSO_3, HSO_4, and H_2PO_4 all had hindered rotations due to an oxygen atom that has two single bonds connecting the oxygen atom, one to the rest of the nucleophile and one to the chlorinated methyl fragment. The effects of these hindered rotations are included in the calculation of $S°$, and account for between 9 and 18 cal/mol-K of their molar entropies. As seen in comparisons between the calculated and experimental values of S° ($CH_3(NO_3)$), where $S°_{hindered}(CH_3(NO_3)) = 9.245$cal/mol-K (MP2/cc-pVDZ), our treatment of hindered rotations yields good results. In addition to the rotations about the oxygen atom, there are also hindered rotations on the species with $N = HCO_3$, HSO_3, HSO_4, and H_2PO_4 due to rotations of the OH group. However, these rotations are much more hindered than the rotations about the other oxygen atom. In this case, the rotation was considered as a torsional oscillation and was included as a normal term in the vibrational contribution to the entropy.

The values of ΔH_f and S in Tables 2 and 4 can be used to calculate the gas-phase standard Gibbs free energy of formation of the CCl_3N, CCl_2HN, and $CClH_2N$ species at a given temperature. This can be done by calculating an entropy of formation, $\Delta S°_f$. This is done by subtracting the entropies of the atomic standard states from the virtual entropy of the species.

TABLE 4: Experimental and Calculated Values of Gas-Phase Standard Virtual Molar Entropies (cal/mol-K)

		$S°$(298.15 K,1 bar)			
compd	exp.	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_3OH		77.123	78.053	78.412	77.967
CCl_2HOH		71.356	72.066	72.269	72.017
$CClH_2OH$		63.029	63.162	63.329	63.205
CH_3OH	57.316[a]	56.706	57.073	57.101	57.068
CCl_3SH		80.514	81.348	81.673	81.220
CCl_2HSH		74.700	75.456	75.691	75.241
$CClH_2SH$		68.886	69.745	71.979	69.978
CH_3SH	60.987[a]	60.409	60.618	60.630	60.614
$CCl_3(NO_3)$		98.665	97.768	99.369	97.814
$CCl_2H(NO_3)$		93.490	93.527	94.632	93.565
$CClH_2(NO_3)$		85.830	86.111	86.846	86.115
$CH_3(NO_3)$	76.123[a]	75.707	75.868	76.375	75.860
$CCl_3(HCO_3)$		98.535	99.217	100.066	99.307
$CCl_2H(HCO_3)$		95.027	95.504	96.130	95.573
$CClH_2(HCO_3)$		87.684	88.022	88.515	88.105
$CH_3(HCO_3)$		78.039	78.362	78.632	78.230
$CCl_3(HSO_3)$		105.099	105.840	107.248	105.741
$CCl_2H(HSO_3)$		100.260	100.128	102.089	100.954
$CClH_2(HSO_3)$		92.596	93.987	94.676	93.635
$CH_3(HSO_3)$		82.766	83.077	83.939	83.142
$CCl_3(HSO_4)$		107.064	107.796	109.083	107.677
$CCl_2H(HSO_4)$		102.827	103.468	104.525	103.342
$CClH_2(HSO_4)$		95.448	95.874	96.654	95.694
$CH_3(HSO_4)$		85.545	85.932	86.595	85.766
$CCl_3(H_2PO_4)$		111.383	112.363	113.005	111.601
$CCl_2H(H_2PO_4)$		106.724	106.358	108.198	107.638
$CClH_2(H_2PO_4)$		99.116	98.653	100.265	99.772
$CH_3(H_2PO_4)$		89.292	89.219	89.649	88.996
CCl_3F	74.030[b]	73.688	74.143	74.594	74.205
CCl_2HF	70.088[b]	69.850	70.139	70.436	70.184
$CClH_2F$	63.196[b]	63.082	63.222	63.393	63.260
CH_3F	53.260[b]	53.202	53.262	53.324	53.258
CCl_4	74.056[a]	73.589	74.141	74.653	74.241
CCl_3H	70.676[a]	70.371	70.727	71.057	70.798
CCl_2H_2	64.587[a]	64.396	64.568	64.763	64.637
$CClH_3$	56.066[a]	55.906	55.980	56.058	56.006
CH_4	44.518[a]	44.518	44.567	44.536	44.487
		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 67. [b] Experimental reference 55.

For example, $\Delta S°_f(CCl_3F)$ and $\Delta G°_f(CCl_3F)$ are calculated from the following expressions:

$$\Delta S°_f(CCl_3F) = S°\ (CCl_3F) - (S°\ (\text{C-graphite}) + 3S°(1/2Cl_2) + S°(1/2F_2))$$

$$\Delta G°_f(CCl_3F) = \Delta H°_f(CCl_3F) - T\Delta S°_f(CCl_3F)$$

For example, by using the MP2/cc-pVDZ values for $S°$ (CCl_3F) and $\Delta H°_f(CCl_3F)$ (isodesmic), the entropy of formation is calculated to be $\Delta S°_f(CCl_3F) = -35.440$ cal/mol-K and the Gibbs free energy of formation is calculated to be $\Delta G°_f(CCl_3F) = -60.94$ kcal/mol, compared to the experimental values of −35.098 cal/mol-K and −58.54 kcal/mol, respectively. A Table of calculated $\Delta G°_f$ values at 298 K is given as Supporting Information.

TABLE 5: Experimental and Calculated Free Energies of Solvation (kcal/mol) for the Chlorinated Methanes and the CCl_3N, CCl_2HN, $CClH_2N$, and CH_3N Species

	ΔG_S(298.15 K, 1 bar)				
	exptl[a]	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_3OH		−1.36	−2.15	−1.71	−1.79
CCl_2HOH		−6.03	−5.96	−5.49	−5.58
$CClH_2OH$		−6.35	−6.79	−6.24	−6.48
CH_3OH	−3.19[a]	−2.81	−3.65	−3.19	−3.34
CCl_3SH		2.92	2.72	3.05	3.16
CCl_2HSH		−0.28	−0.37	−0.06	0.3
$CClH_2SH$		−1.14	−1.37	−1.06	−1.08
CH_3SH		0.74	0.42	0.64	0.71
$CCl_3(NO_3)$		4.28	4.83	5.22	4.98
$CCl_2H(NO_3)$		−1.48	0.75	1.66	0.41
$CClH_2(NO_3)$		−2.11	−1.22	−0.63	−1.42
$CH_3(NO_3)$		−1.36	−0.26	−0.29	−0.97
$CCl_3(HCO_3)$		−3.77	−3.68	−2.80	−3.13
$CCl_2H(HCO_3)$		−4.60	−4.57	−3.85	−5.43
$CClH_2(HCO_3)$		−7.47	−7.30	−6.51	−7.05
$CH_3(HCO_3)$		−5.56	−5.66	−5.26	−5.65
$CCl_3(HSO_3)$		1.84	1.92	2.52	2.25
$CCl_2H(HSO_3)$		0.72	1.67	1.61	0.32
$CClH_2(HSO_3)$		−1.92	−1.58	−1.27	−1.67
$CH_3(HSO_3)$		−0.95	−0.77	−0.41	−0.82
$CCl_3(HSO_4)$		−5.21	−4.75	−3.67	−4.64
$CCl_2H(HSO_4)$		−10.19	−9.84	−7.64	−8.70
$CClH_2(HSO_4)$		−10.20	−9.71	−8.58	−9.35
$CH_3(HSO_4)$		−9.47	−9.07	−7.79	−8.90
$CCl_3(H_2PO_4)$		−4.33	−5.46	−4.12	−4.76
$CCl_2H(H_2PO_4)$		−8.07	−6.12	−7.29	−7.52
$CClH_2(H_2PO_4)$		−7.03	−6.66	−7.19	−7.98
$CH_3(H_2PO_4)$		−8.62	−9.11	−8.12	−8.68
CCl_3F	2.73[b]	4.64	4.72	4.88	4.80
CCl_2HF	0.98[c]	0.92	1.28	1.11	1.21
$CClH_2F$	1.12[c]	0.07	0.40	0.44	0.23
CH_3F	1.57[c]	1.45	1.62	1.66	1.43
CCl_4	1.8[a]	5.04	5.06	5.24	5.20
CCl_3H	0.8[a]	1.46	1.55	1.91	1.54
CCl_2H_2	0.6[a]	0.29	0.45	0.54	0.43
$CClH_3$	1.3[a]	1.42	1.39	1.44	1.36
CH_4	3.9[a]	3.74	3.62	3.66	3.68

[a] Experimental reference 68. [b] Experimental reference 69. [c] Experimental reference 70.

V. Calculation of Free Energies of Solvation

We used the continuum solvation model of Tomasi et al.[38−40,54] to describe the solvation thermodynamics of the CCl_3N, CCl_2HN, $CClH_2N$, and CH_3N species. In this method, the solvation energy is composed of a sum of noncovalent electrostatic, cavitation, dispersion, and repulsion energies. For the electrostatic energy, the solvent, in this case H_2O, is represented by an infinite homogeneous continuous medium having a dielectric constant of 78.3, and the solute is represented by an empty cavity, inside which the solute's electrostatic charge distribution is placed. This approach self-consistently minimizes the electrostatic energy by optimizing the polarization of the continuous medium and charge distribution of the solute. There are many ways to represent the polarization of the continuous medium, and Tomasi et al. use a surface charge representation.[38] The cavitation, dispersion, and repulsion terms are less straightforward to handle because the interactions take place at short distances. In the present method, these terms are converted to surface area integrals from their representations as discrete summations.[61] This is formally done by introducing calibration constants from hard sphere packing and applying the Green−Ostrogradski theorem to convert the volume integrals to surface integrals.[61] In practice, this results in a cavity-dispersion-repulsion free energy function that depends on the surface area surrounding the solute (usually defined by van der Waals radii of the solute atoms) and the position of atoms within the solute cavity. This function is then parameterized by comparison with vaporization and sublimation free energy data. Despite the approximate treatment of solvation in this approach, it and others like it have been shown to give hydration energies of many neutral molecules within a few kcal/mol as compared to experiment.[39,40,62−65]

Table 5 lists the calculated free energies of solvation at various electronic structure levels for the CCl_3N, CCl_2HN, $CClH_2N$, and CH_3N species, along with experimental and calculated data for the chlorinated methanes. A value of 1.90 kcal/mol was added to the calculated free energies, because the standard state in the gas phase in the Tomasi et al. model is 1 mol/L at 298.15 K rather than at 1 bar of pressure at 298.15 K. To perform these calculations, gas-phase geometries were used, and corrections due to the change in internal vibration and rotation were neglected.

The corrections for changes in internal vibrations are expected to be small. However, the corrections for changes in internal rotations may be sizable for the species with hindered rotations and polar substituents. In a worst case scenario, the polar substituent will completely constrain the internal rotations, which could lead to the solvation energies in Table 5 being overstabilized by as much as 2−5 kcal/mol ($S^\circ_{\mathrm{hindered}}(\mathrm{gas}) = 9-18$ cal/mol-K) for the species with hindered rotations ($N = NO_3$, HCO_3, HSO_3, HSO_4, and H_2PO_4).

Considering the approximations in the model, excellent agreement with the available experimental results is found, usually better than 1 kcal/mol, except for CCl_4. This worst case molecule has a small electrostatic term (no dipole), and the majority of its solvation energy comes from the empirical cavity-dispersion-repulsion term, rather than from the electrostatic term.

VI. Calculation of Gibbs Free Energies of Reaction for S_N2 Reactions

Table 6 shows Gibbs free energies of reaction for the following S_N2 reactions:

$$N^-_{(aq)} + CCl_{4(aq)} \rightarrow CCl_3N_{(aq)} + Cl^-_{(aq)}$$

$$N^-_{(aq)} + CHCl_{3(aq)} \rightarrow CHCl_2N_{(aq)} + Cl^-_{(aq)}$$

$$N^-_{(aq)} + CH_2Cl_{2(aq)} \rightarrow CH_2ClN_{(aq)} + Cl^-_{(aq)}$$

$$N^-_{(aq)} + CH_3Cl_{(aq)} \rightarrow CH_3N_{(aq)} + Cl^-_{(aq)}$$

where $N^- = OH^-$, SH^-, NO_3^-, $H_2PO_4^-$, HCO_3^-, HSO_3^-, HSO_4^-, and F^-.

Table 6 was generated by using experimental values for $\Delta G^\circ_f(N^-_{(aq)})$, $\Delta G^\circ_f(Cl^-_{(aq)})$, and $\Delta G^\circ_f(CCl_xH_{y(g)})$ found in Tables 3, 4, and 7, and the remaining values, $\Delta G^\circ_f(CCl_{x-1}H_yN_{(g)})$, $\Delta G_s(CCl_xH_y)$, and $\Delta G_s(CCl_{x-1}H_yN_{(g)})$, were obtained from Tables 2, 4, and 5.

In the calculations summarized in Table 6, the calculated $\Delta G_s(CCl_xH_y)$ solvation values were used rather than the experimental values for consistency. The majority of the calculated solvation energy in these molecules comes from the cavity-dispersion-repulsion term rather than from the electrostatic term. A similar error in the cavity-dispersion-repulsion term is expected to exist for $\Delta G^\circ_f(CCl_{x-1}H_yN_{(g)})$ values. It is expected that introducing calculated $\Delta G_s(CCl_xH_y)$ solvation values will lead to some cancellation of errors in the dispersion-repulsion solvation energies for the reactions.

As expected, the differences in the calculated heats of formation dominated the differences in the calculated ΔG's with

TABLE 6: Heats of Reaction (kcal/mol) for the S_N2 Reactions in the Aqueous Phase

	ΔG_{rxn}				
compd	exp.	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_3OH		−40.84	−41.71	−37.50	−36.27
CCl_2HOH		−36.07	−36.69	−34.88	−33.55
$CClH_2OH$		−28.44	−29.00	−27.81	−27.51
CH_3OH	−23.27				
CCl_3SH		−27.06	−25.99	−22.76	−21.43
CCl_2HSH		−24.34	−24.34	−22.05	−20.45
$CClH_2SH$		−22.55	−22.84	−22.07	−21.14
CH_3SH	−23.44[a]				
CCl_3NO_3		−6.71	−1.25	0.70	4.67
CCl_2HNO_3		−7.58	−3.61	−1.51	0.24
$CClH_2NO_3$		−3.87	−1.63	−0.63	−0.25
CH_3NO_3	−3.81[a]				
$CCl_3(HCO_3)$		−13.16	−12.63	−7.74	−6.37
$CCl_2H(HCO_3)$		−14.16	−13.95	−10.80	−10.57
$CClH_2(HCO_3)$		−14.09	−14.70	−12.34	−11.71
$CH_3(HCO_3)$	−11.39[b]				
$CCl_3(HSO_3)$		−0.67	2.17	4.16	7.18
$CCl_2H(HSO_3)$		2.59	3.33	6.71	7.93
$CClH_2(HSO_3)$		4.78	4.45	5.80	7.15
$CH_3(HSO_3)$	9.09[c]				
$CCl_3(HSO_4)$		17.36	14.53	17.27	18.96
$CCl_2H(HSO_4)$		16.89	12.52	19.29	17.00
$CClH_2(HSO_4)$		16.43	10.97	12.16	12.51
$CH_3(HSO_4)$	14.85[c]				
$CCl_3(H_2PO_4)$		5.59	5.73	11.37	12.94
$CCl_2H(H_2PO_4)$		4.62	6.55	8.65	10.25
$CClH_2(H_2PO_4)$		8.60	7.99	9.91	10.35
$CH_3(H_2PO_4)$	11.11[c]				
CCl_3F	−7.39	−11.60	−12.51	−8.89	−7.34
CCl_2HF	−7.45	−9.28	−10.37	−7.93	−6.05
$CClH_2F$	−4.67	−6.07	−7.01	−5.36	−4.53
CH_3F	−0.94				

[a] MP2/cc-pVDZ values were used for the solvation energy of $\mathrm{CH_3}N$ and $CClH_3$, and experimental values were used for the gas-phase Gibbs free energy of formation of $\mathrm{CH_3}N$ and $CClH_3$. [b] MP2/cc-pVDZ values were used for the solvation energy of $\mathrm{CH_3}N$ and $CClH_3$, experimental value was used for the gas-phase Gibbs free energy of formation of CCl_3H, experimental value was used for the enthalpy of formation of CH3N, and a MP2/cc−pVDZ values was used for the entropy. [c] MP2/cc-pVDZ values were used for the solvation energy of $\mathrm{CH_3}N$ and $CClH_3$. G2 theoretical and MP2/cc-pVDZ values were used respectively for the gas-phase enthalpy and entropy of formation of $\mathrm{CH_3}N$. Experimental value was used for the gas-phase Gibbs free energy of formation of $CClH_3$.

TABLE 7: Experimental Enthalpies and Gibbs Free Energies of Formation (kcal/mol) of the Monovalent Anions in the Aqueous Phase

Compd	ΔH°_f (298.15 K, 1 bar)	ΔG°_f (298.15 K, 1 bar)
Cl^-	−39.952[a]	−31.364[a]
OH^-	−54.970[a]	−37.582[a]
SH^-	−4.207[a]	+2.89[a]
NO_3^-	−49.0[a]	−25.99[a]
HCO_3^-	−165.39[a]	−140.24[a]
HSO_3^-	−149.67[a]	−126.13[a]
HSO_4^-	−212.08[a]	−180.67[a]
$H_2PO_4^-$	−309.82[a]	−270.14[a]
F^-	−79.50[a]	−66.63[a]

[a] Experimental reference 67.

TABLE 8: Enthalpies of Reaction (kcal/mol) for the S_N2 Reactions in the Gas Phase

	ΔH_{rxn}				
compd	exp.	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_3OH		−66.44	−66.22	−62.16	−61.02
CCl_2HOH		−60.92	−61.31	−59.55	−58.57
$CClH_2OH$		−54.46	−54.37	−53.59	−53.20
CH_3OH	−50.24				
CCl_3SH		−25.33	−23.79	−20.61	−19.57
CCl_2HSH		−23.35	−22.94	−20.53	−19.79
$CClH_2SH$		−21.43	−21.08	−19.86	−19.62
CH_3SH	−22.54				
CCl_3NO_3		2.44	7.11	9.32	13.03
CCl_2HNO_3		3.58	5.43	7.31	9.61
$CClH_2NO_3$		7.24	7.81	8.95	9.79
CH_3NO_3	7.08				
$CCl_3(HCO_3)$		−7.12	−6.30	−1.86	−0.42
$CCl_2H(HCO_3)$		−10.38	−9.97	−7.00	−5.72
$CClH_2(HCO_3)$		−8.64	−9.15	−7.35	−6.41
$CH_3(HCO_3)$	−6.70				
$CCl_3(HSO_3)$		5.63	8.63	10.67	13.42
$CCl_2H(HSO_3)$		6.36	6.19	10.58	12.39
$CClH_2(HSO_3)$		9.90	9.80	11.14	12.46
$CH_3(HSO_3)$	14.33				
$CCl_3(HSO_4)$		34.14	31.09	33.31	35.51
$CCl_2H(HSO_4)$		35.18	30.75	36.04	34.03
$CClH_2(HSO_4)$		33.53	27.85	28.25	28.97
$CH_3(HSO_4)$	32.29				
$CCl_3(H_2PO_4)$		5.99	7.57	12.25	13.99
$CCl_2H(H_2PO_4)$		5.16	5.16	9.31	10.6
$CClH_2(H_2PO_4)$		6.83	5.88	8.90	9.87
$CH_3(H_2PO_4)$	12.03				
CCl_3F	−38.93	−41.44	−42.28	−38.50	−37.03
CCl_2HF	−37.57	−38.75	−40.02	−36.97	−35.63
$CClH_2F$	−35.02	−35.71	−36.78	−35.03	−34.14
CH_3F	−31.20				

a worst case error being ~10 kcal/mol for the CCl_3NO_3 species, as expected. Very little difference was seen between the methods in the entropy and solvation calculations.

Our results clearly show that the OH^-, SH^-, HCO_3^-, and F^- nucleophiles are thermodynamically favored and Cl^- should be displaced from the chlorinated methanes. The HSO_4^- and $H_2PO_4^-$ nucleophiles are not thermodynamically favored to displace Cl^-. The reactions of the HSO_3^- nucleophile are predicted to be slightly endothermic to thermoneutral, especially for the more chlorinated species, and it is difficult to tell if Cl^- will be displaced or not without higher level calculations. The reactions of the NO_3^- nucleophile are slightly exothermic, but again our calculations are not accurate enough to distinguish whether Cl^- will be displaced or not. The effect of the degree of chlorination is largely nucleophile dependent, and the OH^- nucleophile shows the largest effect. In this case, the S_N2 reaction generating CCl_3OH is ~15 kcal/mol more favorable than for the reaction generating CH_3OH. The reactions of the other nucleophiles do not greatly depend on the degree of chlorination. In some cases, the more highly chlorinated is the most exothermic, but this trend is reversed in others.

The gas-phase reaction enthalpies are given in Table 8 so that we can investigate the role of solvation. In looking at Table 8 we see that the OH^-, SH^-, and F^- reactions have a strong enthalpic driving force. The HCO_3^- reactions also have an enthalpic driving force, but it is not quite as strong as the other reactions. On the other hand, the NO_3^-, HSO_3^-, HSO_4^-, and $H_2PO_4^-$ reactions do not have an enthalpic driving force. Comparing Tables 6 and 8 we see that the effect of solvent is somewhat correlated to the size of anion with respect to the size of the Cl^- anion. The reactions with the less bulky anions, i.e., OH^- and F^-, are substantially less exothermic as compared to the gas-phase value when the effects of solvent are included, and the reactions with the bulkier anions, i.e., SH^-, NO_3^-, HCO_3^-, HSO_3^-, HSO_4^-, and $H_2PO_4^-$, are substantially more exothermic than the gas-phase values when the effects of solvent are included. However, other parameters besides the charge-to-size ratio must play a role in solvation. While reactions with the least bulky anion, F^-, do have the most endothermic solvent effect, the reactions with the most bulky anion, $H_2PO_4^-$, do not have the most exothermic solvent effect. This suggests that other chemical parameters must play a role in the solvent effect for these reactions.

VII. Conclusion

Our theoretical study of reactions between the chlorinated methanes and the monovalent anions, $N^- = OH^-$, SH^-, NO_3^-, HCO_3^-, HSO_3^-, HSO_4^-, $H_2PO_4^-$, and F^-, shows that the energetics of the nucleophilic displacement reaction are strongly dependent on the nucleophile and less so on the degree of chlorination. Of the nucleophiles studied, the smaller ions OH^-, SH^-, and F^- as well as the larger HCO_3^- ion were the most thermodynamically favored candidates for nucleophilic substitution with the chlorinated methanes. In addition, reactions with the NO_3^- ion are expected to be slightly exothermic to thermoneutral, and those with the HSO_3^- ion are slightly endothermic to thermoneutral. The reactions of the HSO_4^- and $H_2PO_4^-$ are clearly not likely to occur. The degree of chlorination can change the thermodynamics of the nucleophilic reactions by as much as 18 kcal/mol, but only the OH^- nucleophile exhibits such a dramatic effect. For most of the nucleophiles, the calculations indicate that the heat of reaction decreases for the chlorinated methanes with a larger degree of chlorination. The exception was the HSO_4^- nucleophile, which showed a slight increase in the Gibbs free energy of reaction in going from CH_3Cl to CCl_4.

Our results agree with the available experimental data which show that OH^-, SH^-, and F^- do displace Cl^-. The results for the phosphate nucleophile, $H_2PO_4^-$, are not as easy to compare to the available experimental results. Work by Barbash and Reinhard indicates that a phosphate buffer accelerates nucleophilic substitution rates of both 1,2-dichloroethane and 1,2-dibromoethane in water.[8] They suggest that the HPO_4^{2-} nucleophile is responsible for this acceleration (note the difference in the monoanion that we calculated and the dianion from experiment). Further study is needed before concluding that theory and experiment are in disagreement as there are likely to be significant thermodynamic differences between the HPO_4^{2-} and $H_2PO_4^-$ nucleophiles. This is due to differential solvation effects including different hydrogen bonding networks in solution for the monoanion as compared to the dianion. The possibility also exists that the phosphate buffer solution contained increased levels of bicarbonate, which the calculations performed here indicate would be quite important in promoting reaction rates for the halogenated alkanes.

Finally, it is important to emphasize that the thermodynamic quantities presented here are initial studies to determine if a reaction is even allowed or not. Equally important in understanding these reactions are the height and shape of kinetic barriers existing between the reactants and products including the role of solvent on the reaction pathways. We are currently extending our studies to investigate the role of kinetics for these reactions.

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Supporting Information Available: Tables of ab initio total energies and enthalpy corrections for the gas-phase CH_xCl_y and $CH_xCl_{y-1}N$ compounds determined from LDA/DZVP2, BP91/DZVP2, B3LYP/DZVP2, and MP2/cc-pVDZ total energy and vibrational calculations.

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