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Ab Initio Electronic Structure Study of One-Electron Reduction of Polychlorinated Ethylenes

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Polychlorethylene radicals, anions, and radical anions are potential intermediates in the reduction of polychlorinated ethylenes (C_2Cl_4, C_2HCl_3, *trans*-$C_2H_2Cl_2$, *cis*-$C_2H_2Cl_2$, 1,1-$C_2H_2Cl_2$, C_2H_3Cl). Ab initio electronic structure methods were used to calculate the thermochemical properties, ΔH_f°(298.15 K), S°(298.15 K,1 bar), and ΔG_S(298.15 K, 1 bar) of 37 different polychloroethylenyl radicals, anions, and radical anion complexes, $C_2H_yCl_{3-y}^\bullet$, $C_2H_yCl_{3-y}^-$, and $C_2H_yCl_{4-y}^{\bullet-}$ for $y = 0-3$, for the purpose of characterizing reduction mechanisms of polychlorinated ethylenes. In this study, 8 radicals, 7 anions, and 22 radical anions were found to have stable structures, i.e., minima on the potential energy surfaces. This multitude of isomers for $C_2H_yCl_{4-y}^{\bullet-}$ radical anion complexes are π*, σ*, and $-H\cdots Cl^-$ structures. Several stable π* radical anionic structures were obtained for the first time through the use of restricted open-shell theories. On the basis of the calculated thermochemical estimates, the overall reaction energetics (in the gas phase and aqueous phase) for several mechanisms of the first electron reduction of the polychlorinated ethylenes were determined. In almost all of the gas-phase reactions, the thermodynamically most favorable pathways involve $-H\cdots Cl^-$ complexes of the $C_2H_yCl_{4-y}^{\bullet-}$ radical anion, in which a chloride ion is loosely bound to a hydrogen of a $C_2H_xCl_{2-x}^\bullet$ radical. The exception is for C_2Cl_4, in which the most favorable anionic structure is a loose σ* radical anion complex, with a nearly iso-energetic π* radical anion. Solvation significantly changes the product energetics with the thermodynamically most favorable pathway leading to $C_2H_yCl_{3-y}^\bullet + Cl^-$. The results suggest that a higher degree of chlorination favors reduction, and that reduction pathways involving the $C_2H_yCl_{3-y}^-$ anions are high energy pathways.

I. Introduction

The widespread use of polychlorinated ethylenes as solvents has resulted in their ubiquitous presence in the environment. Due to their volatility, these toxic compounds are widely dispersed at low concentrations in the atmosphere.[1] In the subsurface, the immiscibility of the polychlorinated ethylenes leads to pools and ganglia of nonaqueous-phase liquid below a spill site, which then becomes a source for dissolved-phase contamination that can form a very large plume of contaminated groundwater.[2] This sort of contamination is difficult to remediate using extraction technologies such as conventional “pump and treat”, and therefore, there is great interest in situ remediation strategies that degrade polychlorinated ethylenes.[3] Most of these technologies, whether they be chemical and microbiological, rely mainly on reductive reactions for dechlorination of the contaminants.[4]

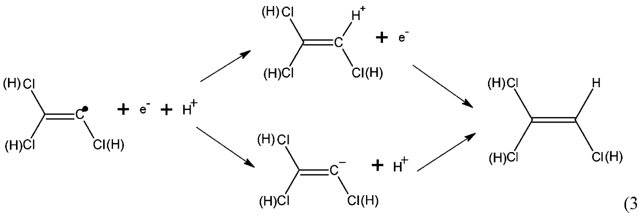
Two likely reductive pathways for polychlorinated ethylenes (as shown in Figure 1) in anaerobic and reducing groundwater environments are hydrogenolysis (eq 1) and elimination (eq 4

$$C_2H_xCl_{4-x} + 2e^- + H^+ \rightarrow C_2H_{x+1}Cl_{3-x} + Cl^- \qquad (1)$$

below).[5] The hydrogenolysis mechanism involves two electrons and a proton and results in the formation of a chloride ion and of a new C−H bond. This two electron transfer (ET) process is assumed to occur in two sequential steps: the first electron transfer to the polychlorinated ethylene is a dissociative electron attachment reaction leading to the formation of a polychloroethylen-1-yl radical and a chloride ion, eq 2. The second ET

$$C_2H_xCl_{4-x} + e^- \rightarrow C_2H_xCl_{3-x}^\bullet + Cl^- \qquad (2)$$

allows the newly formed radical to bind to a proton to form a neutral compound, eq 3. The other mechanism, an elimination reaction, involves two electrons and results in the release of



(3)

two chloride ions and the formation of a double or triple C−C bond (eq 4). This two ET process is also assumed to occur in

$$C_2H_xCl_{4-x} + 2e^- \rightarrow C_2H_xCl_{2-x} + 2Cl^- \qquad (4)$$

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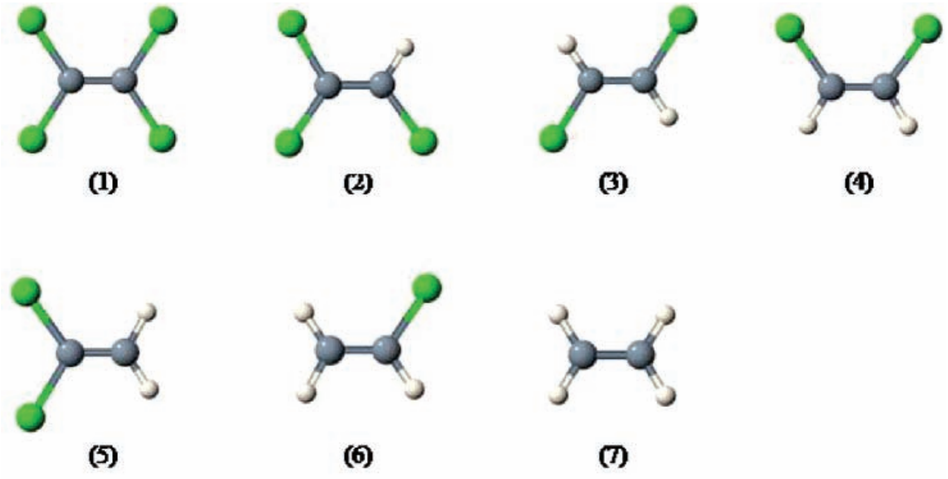
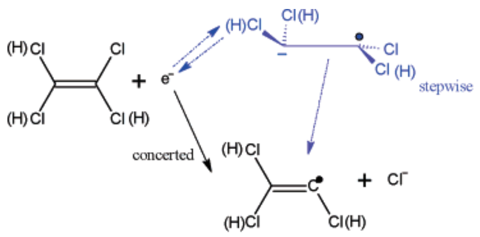


Figure 1. Structures of chloroethylenes.

two sequential steps: the first ET is again the dissociative electron attachment reaction leading to formation of a polychloroethylenyl radical and a chloride ion, as in eq 2. However, the second ET step forms a chloracetylene molecule and a chloride ion, eq 5.

$$C_2H_xCl_{3-x}^{\bullet} + e^- \rightarrow C_2H_xCl_{2-x} + Cl^- \qquad (5)$$

It is believed is that the rate-limiting step in both of these ET reactions is the first electron reduction (eq 2).[6] However, the details of this first ET step are not fully established. Two possible mechanisms have been identified for eq 2: a stepwise mechanism and a concerted mechanism.[6] In the stepwise mechanism, the ET forms a stable radical anion intermediate that subsequently undergoes dissociation. In the concerted mechanism, ET and dissociation occur simultaneously. The distinction between these two mechanisms is illustrated in reaction scheme of eq 6.



(6)

It has recently been suggested by Costentin et al.,[6] on the basis of cyclic voltammetry experiments, that in solution the first electron transfer to tetrachloroethylene, trichloroethylene, and dichlororethylene proceeds via a stepwise mechanism. This suggests the existence of a π* radical anion intermediate. The bonding in this type of intermediate is best described as a 3-electron 2-orbital bond of π character with carbon atoms that are sp^3 hybridized rather than sp^2 hybridized, and a dangling lone pair of electrons on one carbon atom and a radical electron on the other carbon atom. For tetrachloroethylene the existence of the intermediate has been confirmed by several experimental and computational studies.[7-14] However, for trichloroethylene and dichloroethylene the existence of such an intermediate is less certain. Although thermal electron attachment negative ion mass spectrometry gas-phase studies by Chen et al.[11,12] suggest their existence, similar studies by Johnson et al.[10] do not. Moreover, recent ab initio studies fail to find a stable π* radical anion for trichloroethylene[15] and dichloroethylene. This is somewhat surprising because electron transmission spectroscopy studies[7,8,13,14] have unambiguously shown evidence for both Σ and Π anion resonance states, and for the dissociative electron attachment usually proceeding through the Π anion resonance state.[9]

We have been interested in applying the methods of computational chemistry to study the environmental degradation of simple and larger organochlorine compounds.[15-20] In the present study, we use electronic structure methods to investigate the thermochemical properties (in the gas phase and in aqueous solution) for the reaction pathways of polychlorochloroethylenes under reducing conditions. We report thermochemical properties, ΔH_f°(298.15 K), S°(298.15 K,1 bar), ΔG_S(298.15 K, 1 bar) calculated through isodesmic reactions schemes, gas-phase entropy estimates, and continuum solvation models for the polychloroethylenyl radicals and anions shown in Figure 2, and the open shell polychloroethylene radical anions as shown in Figure 3. From these thermochemical data we estimate the energetics of several one-electron reductive pathways. Our objective is not only to elucidate the specific reaction energetics but also to make inferences on reaction kinetics.[21,22] Future work will focus on detailed reaction mechanisms and barriers for these reactions to fully characterize the kinetics.

Our computational approaches are based on accurate ab initio electronic structure methods, but these methods are rarely able to give heat of formation with errors of less than a few kcal/mol[23-26] for a broad class of molecules with more than a few first or second row atoms in the gas phase. Only when very large basis sets such as the correlation-consistent basis sets extrapolated to the complete basis set limit, high level treatments of correlation energy such as coupled cluster methods (CCSD(T)), 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[27-29] (chemical accuracy). Although one can now accurately calculate the heats of formation of molecules with up to 6 first row atoms, such high level calculations are extremely demanding and scale computationally as N^7 for N basis functions with large basis sets. In addition to the issues associated with ab initio electronic structure methods, our objective of being able to predict the thermochemical properties of polychloroethylenyl radicals, anions and radical anion chloride complexes in solution requires

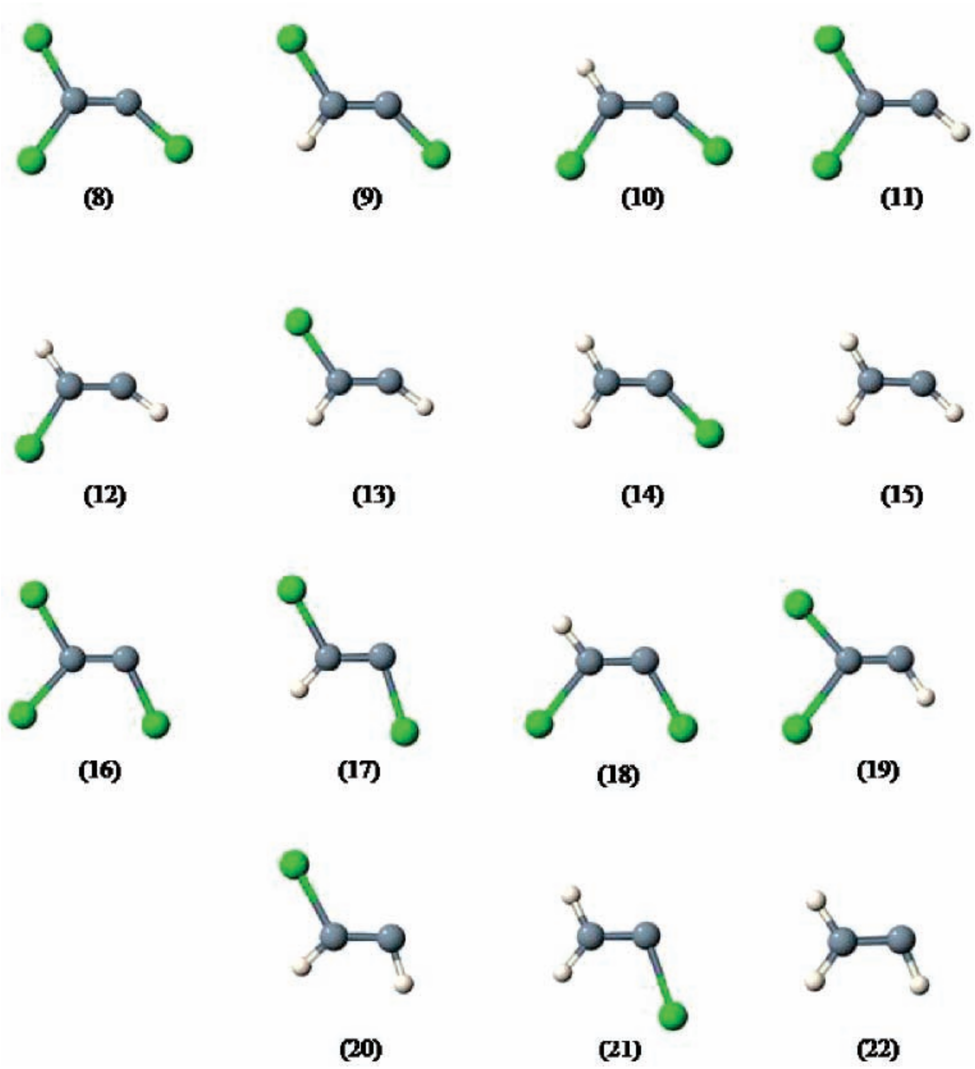


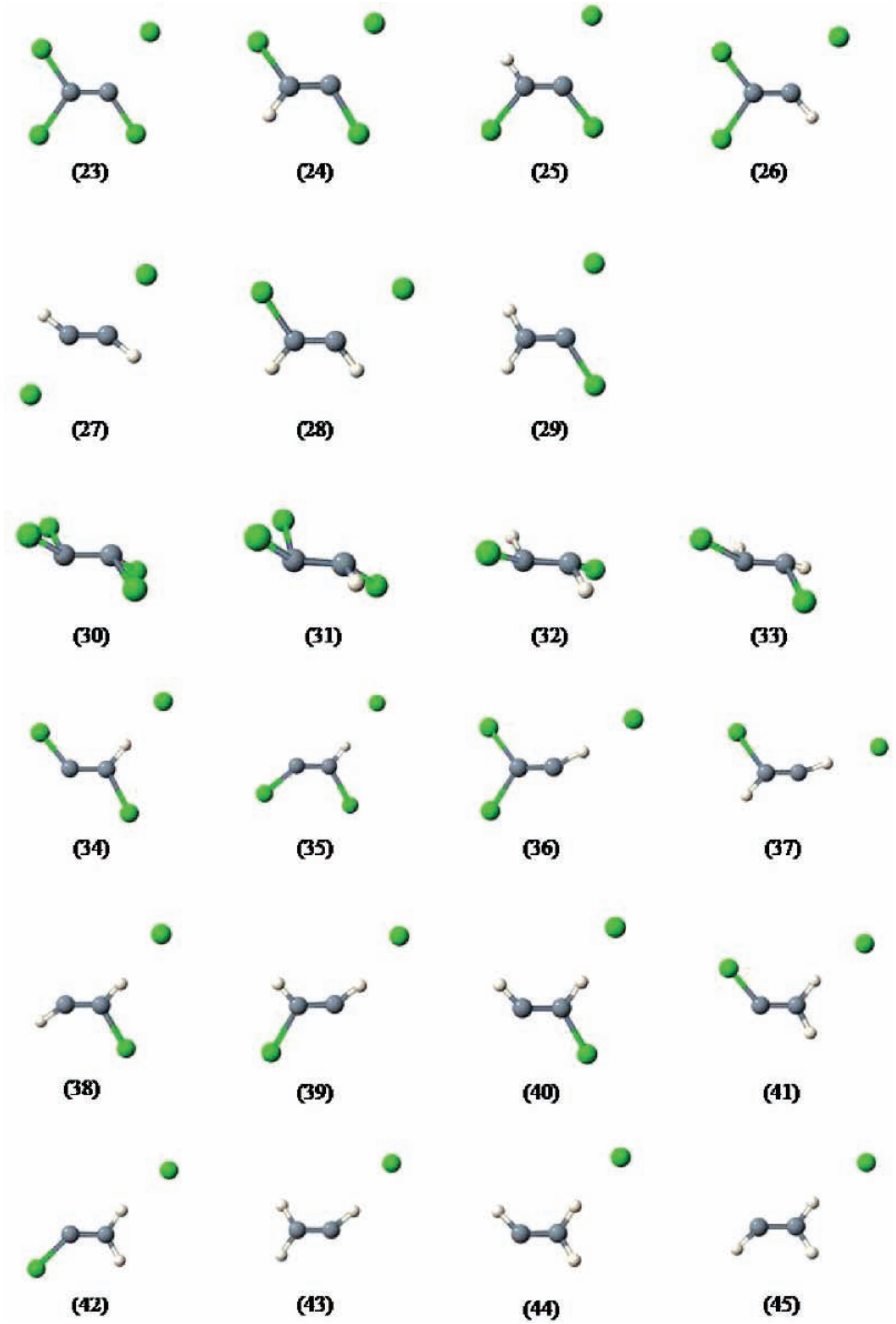
Figure 2. Structures of chlorethylenyl radicals and chlorethylenyl anions.

that solvation contributions be included in addition to the gas-phase thermodynamic properties of heats of formation and entropies.

The computational methods used in this work are described in section II. Calculations for the gas-phase enthalpies of formation, gas-phase entropies, and solvation energies of the radicals and anions: $C_2Cl_3^{\bullet}$, *trans*-1,2-$C_2HCl_2^{\bullet}$, *cis*-1,2-$C_2HCl_2^{\bullet}$, 1,1-$C_2HCl_2^{\bullet}$, *trans*-1,2-$C_2H_2Cl^{\bullet}$, *cis*-1,2-$C_2H_2Cl^{\bullet}$, 1,1-$C_2H_2Cl^{\bullet}$, $C_2H_3^{\bullet}$, $C_2Cl_3^-$, *trans*-1,2-$C_2HCl_2^-$, *cis*-1,2-$C_2HCl_2^-$, 1,1-$C_2HCl_2^-$, *trans*-1,2-$C_2H_2Cl^-$, *cis*-1,2-$C_2H_2Cl^-$, 1,1-$C_2H_2Cl^-$, and $C_2H_3^-$ are reported in section III. The difficulties associated with calculating absolute heats of formation from atomization energies are somewhat alleviated by using a strategy based on isodesmic reactions, one that we adopt below. The gas-phase entropies are estimated using standard statistical mechanical expressions for the vibrational, rotational, and translational entropy contributions, and the solvation energies are estimated using the COSMO continuum solvation model. Similarly, section IV reports calculations for the gas-phase enthalpies of formation, gas-phase entropies, and solvation energies the energies for 23 polychloroethylene radical anion complexes. The results are collected and discussed in section V to provide estimates of thermodynamic properties for the reaction pathways of polychloroethylenes under reducing conditions, and concluding remarks are given in section VI.

II. Ab Initio and Continuum Solvation Calculations

All of the ab initio calculations in this study were performed with the NWChem,[30] Gaussian-98,[31] and MolPro[32] program suites unless noted below. The gas-phase geometries for the neutral, radical, and anionic compounds were optimized and harmonic frequency vibrations were determined. Tables SM-1−SM-8 of the Supporting Information contain the electronic energies, and the thermal vibration energies at 298.15 K for all of the compounds calculated in this study. Most of the ab initio calculations in this study were performed using Density Functional Theory (DFT)[33] calculations and second-order Møller−Plesset perturbation theory (MP2) calculations.[34] The Kohn−Sham equations of DFT[35] were solved using the local density approximation (LDA),[36] and the gradient corrected PBE96,[37] and B3LYP[38,39] exchange-correlation functionals. DFT calculations were performed using the 6-311++G(2d,2p) basis set.[40,41] Similarly, MP2 calculations used the 6-311++G(2d,2p) basis set. We used the spin-unrestricted forms of DFT and other correlation methods, except when noted explicitely. In all cases, the spin contamination was found to be small. To verify the accuracy of various calculations in this study, high accuracy restricted open shell coupled-cluster calculations (RCCSD(T))[42,43] and G3(MP2)[24] calculations were also performed. RCCSD(T) calculations were done using the optimized B3LYP/6-311++G(2d,2p) geometries and used the aug-cc-pVTZ basis



(23) (24) (25) (26)

(27) (28) (29)

(30) (31) (32) (33)

(34) (35) (36) (37)

(38) (39) (40) (41)

(42) (43) (44) (45)

Figure 3. Structures of chlorethylene radical anion complexes.

set.[44] The MolPro program suite was used to perform the RCCSD(T) calculations, and the Gaussian-98 program suite was used to perform the G3(MP2) calculations. The accuracy of G3-(MP2) is quite good and it reproduces experimental atomization energies to within a few kcal/mol for a large number of organic molecules.[24]

Solvation energies for stable solutes in aqueous phase can be approximated as a sum of electrostatic, cavitation, and dispersion energy contributions. The electrostatic contribution to the solvation energies can be estimated using the self-consistent reaction field theory of Klamt and Schüürmann (COSMO),[45] with the cavity defined by the united atom model.[46] The dielectric constant of water used for all of the solvation calculations was 78.4. This continuum model can be used with a variety of ab initio electronic structure calculations in the NWChem program suite including LDA, PBE96, and B3LYP. Calculated gas-phase geometries were used to perform these calculations. The solvent cavity was generated from the surface of nonoverlapping spheres that were discretized by an iterative refinement of triangles starting from a regular octahedron. Three

TABLE 1: Gas-Phase Standard Enthalpies of Formation (kcal/mol) from Isodesmic Reactions and Gas-Phase Enthalpies of Formation Estimates Based on Atomization Energies at the G3MP2 Level[a]

	ΔH_f°(298.15 K) (isodesmic)						ΔH_f°(298.15 K) (atomization)
	LDA[b]	PBE96[b]	B3LYP[b]	MP2[b]	RCCSD(T)[c]	G3MP2	G3MP2
				Radicals			
(8) $C_2Cl_3^\bullet$	53.20	52.69	53.20	58.35	55.28	55.48	55.31
(9) *trans*-$C_2HCl_2^\bullet$	58.29	58.31	58.86	62.32	59.98	60.03	59.47
(10) *cis*-$C_2HCl_2^\bullet$	57.74	57.29	57.78	61.57	59.29	59.27	57.44
(11) 1,1-$C_2HCl_2^\bullet$	62.52	61.68	61.60	64.45	62.74	63.15	62.12
(12) *trans*-$C_2H_2Cl^\bullet$	67.76	66.91	66.71	68.21	67.42	67.57	65.27
(13) *cis*-$C_2H_2Cl^\bullet$	68.84	68.24	68.08	69.25	68.50	68.69	66.38
(14) 1,1-$C_2H_2Cl^\bullet$	62.62	62.82	63.51	65.57	64.22	64.03	61.73
(15) $C_2H_3^\bullet$							70.49
				Anions			
(16) $C_2Cl_3^-$	−4.27	−5.91	−7.14	−3.86	−5.06	−6.78	−8.85
(17) *trans*-$C_2HCl_2^-$	9.27	7.81	5.64	8.18	7.11	6.07	3.61
(18) *cis*-$C_2HCl_2^-$	7.44	5.32	4.47	7.57	6.98	5.44	1.71
(19) 1,1-$C_2HCl_2^-$	10.81	*d*	*d*	*d*	*d*	*d*	*d*
(20) *trans*-$C_2H_2Cl^-$	*d*	*d*	*d*	*d*	*d*	*d*	*d*
(21) *cis*-$C_2H_2Cl^-$	*d*	*d*	*d*	31.72	*d*	*d*	*d*
(22) 1,1-$C_2H_2Cl^-$	26.87	25.28	23.36	25.36	24.77	23.70	19.49
(23) $C_2H_3^-$							53.79

[a] Experimental and ab initio total energy values used to determine these enthalpies of formations are given in Tables A1 and A2 and as Supporting Information. All quantities are in kcal/mol. See text for definitions of isodesmic exchange reactions. [b] 6-311++G(2d,2p) basis set used. [c] aug-cc-pVTZ basis set used. [d] Structure converted to ethyne + Cl^-.

refinement levels, which is equivalent to 128 points per sphere, were used to define the solvent cavity in these calculations. The cavitation and dispersion contributions to the solvation energy were calculated using the methods contained in the Gaussian 98 program package.[31] The approach here estimates these terms using expressions derived from statistical mechanical models of fluids, where the dispersion and repulsion contributions are calculated using the method of Floris et al.[47] and the cavity formation contribution is calculated using the scaled particle theory of Pierotti.[48] 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.[49−51]

III. Polychloroethylenyl Radicals and Polychloroethylenyl Anions

The enthalpies of formation for the gas-phase radicals, $C_2H_xCl_{3-x}^\bullet$, for $x = 0-2$, were calculated using an isodesmic strategy based on the hydrogen exchange reaction.

$$C_2H_{x+1}Cl_{3-x} + C_2H_3^\bullet \rightarrow C_2H_xCl_{3-x}^\bullet + C_2H_4 \qquad (7)$$

The same approach was used by Kumaran et al.[52] and Bylaska et al.[17] for chloromethyl radicals and substituted chloromethyl radicals. Similarly, the enthalpies of formation for the gas-phase anionic $C_2H_xCl_{3-x}^-$ compounds considered in this study were calculated by using an isodesmic strategy based on the acidity reaction.

$$C_2H_{x+1}Cl_{3-x} + C_2H_3^- \rightarrow C_2H_xCl_{3-x}^- + C_2H_4 \qquad (8)$$

The defining property of an isodesmic reaction[53]—that there be an equal number of like bonds on the left-hand and right-hand sides of the reaction—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 estimating direct bonding interactions 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 in the shape of the radical electron (electron pair), as the degree of chlorination is increased from $C_2H_3^\bullet$ ($C_2H_3^-$) to $C_2Cl_4^\bullet$ ($C_2Cl_4^-$) compounds. 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 may reduce the cancellation of errors that is sought in the isodesmic strategy. However, the accuracy obtained previously by Kumaran et al.[52] and Bylaska et al.[17] as well as other researchers, suggests 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.

After the isodesmic reaction energies were determined at a consistent level of theory, the enthalpies of formation of the unknown $C_2H_xCl_{3-x}^\bullet$, and $C_2H_xCl_{3-x}^-$ compounds were calculated using Hess's law (eqs 9 and 10). 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 of $C_2H_3^\bullet$, $C_2H_3^-$, C_2H_4, and $C_2H_{x+1}Cl_{3-x}$ are known, either from experiment or high quality ab initio estimates.

$$\Delta H_f(C_2H_xCl_{3-x}^\bullet) = \Delta H_f^{exp}(C_2H_3^\bullet) + \Delta H_f^{exp}(C_2H_{x+1}Cl_{3-x}) - \Delta H_f^{exp}(C_2H_4) + \Delta H_{rxn}^{isodesmic} \qquad (9)$$

$$\Delta H_f(C_2H_xCl_{3-x}^-) = \Delta H_f^{exp}(C_2H_3^-) + \Delta H_f^{exp}(C_2H_{x+1}Cl_{3-x}) - \Delta H_f^{exp}(C_2H_4) + \Delta H_{rxn}^{isodesmic} \qquad (10)$$

The gas-phase enthalpies of formation, ΔH_f°(298.15 K), for $C_2H_xCl_{3-x}^\bullet$, and $C_2H_xCl_{3-x}^-$ are reported in Table 1. ΔH_f°(298.15 K) obtained for $C_2H_xCl_{3-x}^\bullet$ are in excellent agree-

TABLE 2: Calculated Values of Gas-Phase Standard Molar Entropies (cal mol^{-1} K^{-1})

	$S°$(298.15 K)				
	LDA[a]	PBE96[a]	B3LYP[a]	MP2[a]	exp
Radicals					
(8) $C_2Cl_3^\bullet$	79.94	80.13	79.70	78.50	
(9) *trans*-$C_2HCl_2^\bullet$	72.40	72.47	72.19	71.40	
(10) *cis*-$C_2HCl_2^\bullet$	72.48	72.55	72.24	71.57	
(11) 1,1-$C_2HCl_2^\bullet$	72.27	72.29	71.85	71.03	
(12) *trans*-$C_2H_2Cl^\bullet$	64.78	64.83	64.48	63.98	
(13) *cis*-$C_2H_2Cl^\bullet$	64.76	64.66	64.29	63.73	
(14) 1,1-$C_2H_2Cl^\bullet$	64.04	64.12	63.92	63.53	
(15) $C_2H_3^\bullet$	55.98	55.94	55.76	55.56	
Anions					
(16) $C_2Cl_3^-$	78.49	79.22	78.76	77.98	
(17) *trans*-$C_2HCl_2^-$	71.15	71.67	71.63	70.94	
(18) *cis*-$C_2HCl_2^-$	71.86	72.72	72.33	71.23	
(19) 1,1-$C_2HCl_2^-$	72.90	*d*	*d*	*d*	
(20) *trans*-$C_2H_2Cl^-$	*d*	*d*	*d*	*d*	
(21) *cis*-$C_2H_2Cl^-$	*d*	*d*	*d*	63.50	
(22) 1,1-$C_2H_2Cl^-$	63.35	63.79	63.98	63.28	
(23) $C_2H_3^-$	54.47	54.49	54.38	54.36	
Neutrals					
(1) C_2Cl_4	81.57	82.04	81.54	81.18	81.53[c]
(2) C_2HCl_3	77.66	77.99	77.62	77.35	77.63[c]
(3) *trans*-$C_2H_2Cl_2$	69.47	69.67	69.39	69.23	69.31[c]
(4) *cis*-$C_2H_2Cl_2$	69.20	69.43	69.16	69.01	69.22[c]
(5) 1,1-$C_2H_2Cl_2$	68.84	69.04	68.78	68.62	69.07[c]
(6) C_2H_3Cl	63.06	63.15	62.98	62.90	63.10[c]
(7) C_2H_4	52.40	52.40	52.26	52.32	52.48[c]

[a] 6-311++G(2d,2p) basis set used. [b] aug-cc-pVTZ basis set used. [c] Wagman et al.[56] [d] Structure converted to ethyne + Cl-.

ment with the CHEMKIN Thermodynamic Data Base.[54] Geometry optimization calculations for several of the anion compounds led to charge-dipole complexes containing a chloracetylene and a chloride. ΔH_f°(298.15 K) is not reported for these complexes. The first six columns of this table contain the ΔH_f°(298.15 K) values for the radical compounds and anionic compounds) based on the isodesmic approach using LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), B3LYP/6-311++G-(2d,2p), MP2/6-311++G(2d,2p), RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p), and G3MP2, with the G3MP2 heats of formation given in the last column. The various ab initio 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 12−13 are given in Table A1. For the radical compounds, the average absolute differences from the G3MP2 isodesmic data are 1.13, 1.47, 1.21, 1.64, and 0.17 kcal/mol for the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) methods, respectively, whereas for anionic compounds they are 2.72, 1.08, 0.53, 2.20, and 1.34 kcal/mol for the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), B3LYP/6-311++G(2d,2p), MP2/6-311++G-(2d,2p), and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) methods, respectively. The small differences seen between ab initio methods indicate that the isodesmic strategy is reasonably accurate even when cost-effective/lower level ab initio methods (e.g., B3LYP/6-311++G(2d,2p)) are used. We note that for the $C_2H_xCl_{3-x}^\bullet$ compounds the largest difference from the G3MP2 values are at the MP2 level, whereas for the $C_2H_xCl_{3-x}^-$ compounds the largest differences from the G3MP2 values are at the LDA level. The worst-case difference was ∼5.7 kcal/mol and it is between the PBE96/6-311++G(2d,2p) and MP2/6-311++G(2d,2p) for $C_2Cl_3^\bullet$.

TABLE 3: SCRF Calculated Free Energies of Solvation (kcal/mol)[a]

	ΔG_{SCRF}				
	LDA[a]	PBE96[a]	B3LYP[a]	MP2[a]	exp
Radicals					
(8) $C_2Cl_3^\bullet$	4.89	5.07	5.02	4.81	
(9) *trans*-$C_2HCl_2^\bullet$	2.75	2.95	2.94	2.86	
(10) *cis*-$C_2HCl_2^\bullet$	3.06	3.23	3.23	2.83	
(11) 1,1-$C_2HCl_2^\bullet$	3.71	3.86	3.79	3.47	
(12) *trans*-$C_2H_2Cl^\bullet$	2.04	2.22	2.19	2.14	
(13) *cis*-$C_2H_2Cl^\bullet$	1.70	1.91	1.89	1.85	
(14) 1,1-$C_2H_2Cl^\bullet$	3.46	3.60	3.65	3.51	
(15) $C_2H_3^\bullet$	2.89	3.09	3.13	3.22	
Anions					
(16) $C_2Cl_3^-$	−47.68	−46.82	−47.33	−48.06	
(17) *trans*-$C_2HCl_2^-$	−52.89	−52.16	−52.02	−52.53	
(18) *cis*-$C_2HCl_2^-$	−52.16	−51.64	−51.42	−53.03	
(19) 1,1-$C_2HCl_2^-$	−48.99	*d*	*d*	*d*	
(20) *trans*-$C_2H_2Cl^-$	*d*	*d*	*d*	*d*	
(21) *cis*-$C_2H_2Cl^-$	*d*	*d*	*d*	−57.90	
(22) 1,1-$C_2H_2Cl^-$	−57.93	−57.23	−57.36	−58.06	
(23) $C_2H_3^-$	−68.68	−68.17	−68.61	−69.74	
Neutrals					
(1) C_2Cl_4	5.30	5.47	5.37	5.15	4.4[e]
(2) C_2HCl_3	3.10	3.29	3.23	2.86	4.1[e]
(3) *trans*-$C_2H_2Cl_2$	1.27	1.55	1.47	1.33	3.6[e]
(4) *cis*-$C_2H_2Cl_2$	0.81	1.02	0.94	0.41	4.1[e]
(5) 1,1-$C_2H_2Cl_2$	3.77	3.86	3.79	3.51	4.7[e]
(6) C_2H_3Cl	1.99	2.14	2.09	1.87	4.7[e]
(7) C_2H_4	3.22	3.33	3.32	3.17	5.9[e]

[a] 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. [b] 6-311++G(2d,2p) basis set used. [c] aug-cc-pVTZ basis set used. [d] Structure converted to chloracetylene + Cl$^-$. [e] Totten and Roberts.[57]

Table 2 lists calculated values of $S°$ at 298.15 K for the gas-phase $C_2H_xCl_{3-x}^\bullet$ and $C_2H_xCl_{3-x}^-$ compounds considered in this study. Excellent agreement is found between the calculated values, previous calculations, and known experimental values, with errors not exceeding 1 cal/(mol K) (($T\Delta S$) < 0.5 kcal/mol at $T \sim 300$ K). 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 by calculating the entropy of formation, ΔS_f°, found by subtracting off the entropies of the atomic standard states (Table A3) from the entropy of the compounds. For example, $\Delta S_f^\circ(C_2Cl_3^\bullet)$ and $\Delta G_f^\circ(C_2Cl_3^\bullet)$ are calculated from the following expressions:

$$\Delta S_f^\circ(C_2Cl_3^\bullet) = S^\circ(C_2Cl_3^\bullet) - (2S^\circ(\text{C-graphite}) + 3S^\circ({}^1/_2Cl_2)) \qquad (11)$$

$$\Delta G_f^\circ(C_2Cl_3^\bullet) = \Delta H_f^\circ(C_2Cl_3^\bullet) - T\Delta S_f^\circ(C_2Cl_3^\bullet) \qquad (12)$$

For example, by using the B3LYP/6-311++G(2d,2p) values for $S°(C_2Cl_3^\bullet)$ and $\Delta H_f^\circ(C_2Cl_3^\bullet)$ (isodesmic), the entropy of formation is calculated to be $\Delta S_f^\circ(C_2Cl_3^\bullet) = -6.58$ cal/(mol K) and the Gibbs free energy of formation is calculated to be $\Delta G_f^\circ(C_2Cl_3^\bullet) = 55.16$ kcal/mol. A table of calculated ΔG_f°'s at 298 K is given as Supporting Information.

Table 3 lists the free energies of solvation calculated using SCRF theory 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 characteristics of the radical $C_2H_xCl_{3-x}^\bullet$ and the anionic $C_2H_xCl_{3-x}^-$ compounds

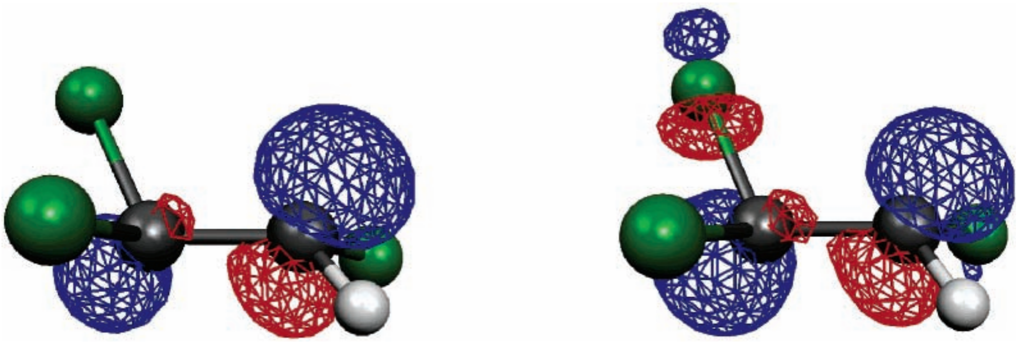


Figure 4. Highest occupied molecular orbital (left, ROHF/6-311++G(2d,2p) calculation; right, LSDA/6-311++G(2d,2p) calculation) for the π^* structure of $C_2HCl_3^-$.

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. Considering the approximations in the model, excellent agreement with the available experimental results is found, usually within a few kcal/mol. 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. 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 (standard state correction) 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.[55,56] For the SCRF theory calculations to conform to this standard state, the following equation (13) should be used:

$$\Delta G_f^\circ(X_{(aq)}^-) = \Delta G_{SCRF}(X^-) + \Delta G_f^\circ(X_{(g)}^-) + 100.18\ \text{kcal mol}^{-1} \quad (13)$$

IV. Polychloroethylene Radical Anion Complexes

Geometry optimization calculations for the polychlorethylene radical anion complexes yielded three π^*, seven σ^*, and twelve $-H\cdots Cl^-$ structures that were stable. UMP2 and G3(MP2) calculations were not performed for these molecular species because the UHF reference wave function contained a significant amount of spin-contamination. The various structures obtained are shown in Figure 3. In contrast to the recent work of Nonnenberg et al.,[15] our calculations yielded stable (i.e., local minima with no imaginary frequencies) π^* structures for $C_2HCl_3^{\bullet-}$ and *trans*-1,2-$C_2H_2Cl_2^{\bullet-}$. The difference in our results can be explained by the fact that Nonnenberg et al. only used a UDFT level of theory. Optimizing $C_2Cl_4^{\bullet-}$ with UDFT and UHF resulted in a stable π^* structure, whereas for $C_2HCl_3^{\bullet-}$ and *trans*-1,2-$C_2H_2Cl_2^{\bullet-}$ a stable π^* structure could not be found and the optimization always resulted in a σ^* structure. We attribute this to the spin contamination. As shown in Figure 4, the ROHF → UHF instability results in a highest occupied molecular orbital that contains a significant amount of symmetry breaking mixing between the π^*-like and σ^*_{C-Cl} orbitals, which in turn results in an unstable structure. Only by using ROHF were we able to attain a stable π^* structure for $C_2HCl_3^{\bullet-}$, and *trans*-1,2-$C_2H_2Cl_2^{\bullet-}$.

The enthalpies of formation for the various σ^*, π^*, and $-H\cdots Cl^-$ radical anions were calculated using the following isodesmic reactions that separate out the bonding and nonbonding interactions:

$$Cl^-\cdots C_2H_xCl_{3-x} + CCl_4 \rightarrow C_2H_xCl_{4-x} + CCl_4^- \quad (14)$$

$$C_2H_xCl_{4-x}^- + 2C_2H_6 \rightarrow C_2H_{2+x}Cl_{4-x} + C_2H_5^- + C_2H_5^\bullet \quad (15)$$

$$C_2Cl_{2-x}H_{1+x}\cdots Cl^- + CH_4 + C_2H_4 \rightarrow CH_4\cdots Cl^- + C_2H_3 + C_2H_{2+x}Cl_{2-x} \quad (16)$$

Equation 14 was used to estimate the enthalpies of formation of the gas-phase σ^* radical anions. This isodesmic reaction was chosen because the CCl_4^- radical anion has an electronic structure similar to that of σ^* radical anions, it is essentially a $CCl_3^\bullet$ radical bound to a chloride as a result of a charge-dipole interaction. For the π^* radical anions, eq 15 was used to calculate the enthalpies of formation. This reaction contains an equal number of like C−C, C−H, and C−Cl bonds on the left and right-hand sides of the reaction. It also contains a dangling lone pair ($C_2H_5^-$) and radical ($C_2H_5^\bullet$) on the right-hand side of eq 15 to cancel out the lone pair and radical of the π^* radical anion ($C_2H_xCl_{4-x}^-$). Finally, for the $-H\cdots Cl^-$ structures, in which a chloride ion is loosely bound to the hydrogen of a $C_2H_xCl_{2-x}^\bullet$ radical, eq 16 was used to estimate the enthalpy of formation.

Table 4 contains the values for the enthalpy of formation based on the isodesmic reactions at the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), B3LYP/6-311++G(2d,2p), and RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) levels. The various ab initio energies needed for the isodesmic calculations are given as Supporting Information and the experimental enthalpies of formation of CH_4, C_2H_4, C_2H_6, $C_2H_{2+x}Cl_{2-x}$, and $C_2H_{2+x}Cl_{4-x}$, $C_2H_3^\bullet$, $C_2H_5^\bullet$, CCl_4^-, $C_2H_5^-$, and $CH_4\cdots Cl^-$, are given in Table A1. For the σ^* and π^* radical anions the calculated heats of formation between the DFT methods are similar with differences on the order of a 1 kcal/mol. Good agreement is also seen between the DFT and RCCSD(T) levels for the σ^* radical anions. For the π^* radical anions slightly larger differences are seen between the DFT and RCCSD(T) levels. For the σ^* radical anions, the average absolute differences from the RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) isodesmic data were 1.63, 2.05, and 1.66 kcal/mol for the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), and B3LYP/6-311++G(2d,2p) methods, respectively, whereas for π^* radical

TABLE 4: Gas-Phase Standard Enthalpies of Formation (kcal/mol) from Isodesmic Reactions[a]

	ΔH_f°(298.15 K) (isodesmic)			
	LDA[b]	PBE96[b]	B3LYP[b]	RCCSD(T)[c,d]
	*σ** Structures			
(23) $C_2Cl_3\cdots Cl^-$	−11.43	−10.33	−10.39	−11.74
(24) *trans*-$C_2HCl_2\cdots Cl^-$	−4.44	−3.98	−3.98	−6.42
(25) *cis*-$C_2HCl_2\cdots Cl^-$	−9.08	−8.96	−9.06	−10.42
(26) 1,1-$C_2HCl_2\cdots Cl^-$	*e*	*e*	−3.49	−4.20
(27) *trans*-$C_2H_2Cl\cdots Cl^-$	−3.34	−2.84	−1.63	−0.70
(28) *cis*-$C_2H_2Cl\cdots Cl^-$	10.41	11.38	11.78	9.79
(29) 1,1-$C_2H_2Cl\cdots Cl^-$	5.64	5.98	5.60	2.72
$C_2H_3\cdots Cl^-$	*g*	*g*	*g*	*g*
	*π** Structures			
(30) $C_2Cl_4^-$	−15.25	−14.66	−14.88	−8.45
(31) $C_2HCl_3^-$	−4.98[f]	−4.23[f]	−4.30[f]	1.10[f]
(32) *trans*-$C_2H_2Cl_2^-$	13.80[f]	15.25[f]	14.73[f]	18.25[f]
(33) *cis*-$C_2H_2Cl_2^-$	*h*	*h*	*h*	*h*
1,1-$C_2H_2Cl_2^-$	*h*	*h*	*h*	*h*
$C_2H_4^-$	*h*	*h*	*h*	*h*
	$-H-Cl^-$ Structures			
(34) *trans*-$C_2HCl_2^{\bullet}\cdots Cl^-$	−19.61	−16.48	−12.27	−10.42
(35) *cis*-$C_2HCl_2^{\bullet}\cdots Cl^-$	−16.30	−14.04	−11.18	−10.03
(36) 1,1-$C_2HCl_2^{\bullet}\cdots Cl^-$	−15.57	−13.83	−11.58	−9.44
(37) *trans*-$C_2H_2Cl^{\bullet}\cdots$*cis*-Cl^-	−6.28	−4.87	−3.15	−1.19
(38) *trans*-$C_2H_2Cl^{\bullet}\cdots$iso-Cl^-	−5.13	−2.76	−0.43	0.67
(39) *cis*-$C_2H_2Cl^{\bullet}\cdots$*trans*-Cl^-	−6.61	−4.82	−2.90	−1.22
(40) *cis*-$C_2H_2Cl^{\bullet}\cdots$iso-Cl^-	−6.88	−3.92	−0.91	0.08
(41) 1,1-$C_2H_2Cl^{\bullet}\cdots$*cis*-Cl^-	−9.49	−6.77	−3.06	−1.33
(42) 1,1-$C_2H_2Cl^{\bullet}\cdots$*trans*-Cl^-	−6.48	−4.15	−1.73	−0.94
(43) $C_2H_3^{\bullet}\cdots Cl^-$	3.92	5.81	7.14	7.30
(44) $C_2H_3^{\bullet}\cdots Cl^-$	2.51	5.29	7.57	8.09
(45) $C_2H_3^{\bullet}\cdots Cl^-$	5.49	7.79	9.32	9.42

[a] Experimental and ab initio total energy values used to determine these enthalpies of formations are given in Tables 9 and 10 and as Supporting Information. All quantities are in kcal/mol. See text for definitions of isodesmic exchange reactions. [b] 6-311++G(2d,2p) basis set was used. [c] aug-cc-pVTZ basis set was used. [d] B3LYP/6-311++G(2d,2p) geometry and its corresponding vibration partition function were used. [e] Structure converted to *cis*-$C_2HCl_2\cdots Cl^-$. [f] ROHF/6-311++G(2d,2p) geometry and its corresponding vibration partition function were used. [g] Stable *σ** structure not found. [h] Stable *π** structure not found.

TABLE 5: Calculated Values of Gas-Phase Standard Molar Entropies (cal mol^{-1} K^{-1})[a]

	S°(298.15 K)			
	LDA[b]	PBE96[b]	B3LYP[b]	ROHF
	*σ** Structures			
(23) $C_2Cl_3\cdots Cl^-$	90.798	96.097	92.183	93.671
(24) *trans*-$C_2HCl_2\cdots Cl^-$	83.105	84.769	85.748	90.310
(25) *cis*-$C_2HCl_2\cdots Cl^-$	88.659	87.125	85.793	86.888
(26) 1,1-$C_2HCl_2\cdots Cl^-$	88.760	87.178	86.511	86.067
(27) *trans*-$C_2H_2Cl\cdots Cl^-$	78.668	79.090	79.827	80.042
(28) *cis*-$C_2H_2Cl\cdots Cl^-$	76.251	77.718	79.420	79.970
(29) 1,1-$C_2H_2Cl\cdots Cl^-$	78.733	78.67	77.731	81.269
$C_2H_3\cdots Cl^-$	*c*	*c*	*c*	*c*
	*π** Structures			
(30) $C_2Cl_4^-$	88.851	89.31	88.384	86.651
(31) $C_2HCl_3^-$	*d*	*d*	*d*	80.641
(32) *trans*-$C_2H_2Cl_2^-$	*d*	*d*	*d*	72.766
(33) *cis*-$C_2H_2Cl_2^-$	*c*	*d*	*d*	*d*
1,1-$C_2H_2Cl_2^-$	*d*	*d*	*d*	*d*
$C_2H_4^-$	*d*	*d*	*d*	*d*
	$-H-Cl^-$ Structures			
(34) *trans*-$C_2HCl_2^{\bullet}\cdots Cl^-$	86.825	85.973	86.579	86.056
(35) *cis*-$C_2HCl_2^{\bullet}\cdots Cl^-$	85.932	86.319	87.344	86.834
(36) 1,1-$C_2HCl_2^{\bullet}\cdots Cl^-$	86.603	86.629	87.173	86.850
(37) *trans*-$C_2H_2Cl^{\bullet}\cdots$*cis*-Cl^-	79.289	79.556	80.032	79.890
(38) *trans*-$C_2H_2Cl^{\bullet}\cdots$iso-Cl^-	79.601	78.885	79.367	79.377
(39) *cis*-$C_2H_2Cl^{\bullet}\cdots$*trans*-Cl^-	79.562	79.109	79.483	79.475
(40) *cis*-$C_2H_2Cl^{\bullet}\cdots$iso-Cl^-	79.822	77.830	78.319	78.556
(41) 1,1-$C_2H_2Cl^{\bullet}\cdots$*cis*-Cl^-	81.116	77.979	78.627	78.404
(42) 1,1-$C_2H_2Cl^{\bullet}\cdots$*trans*-Cl^-	81.096	78.196	79.138	78.976
(43) $C_2H_3^{\bullet}\cdots Cl^-$	72.836	70.535	71.084	70.852
(44) $C_2H_3^{\bullet}\cdots Cl^-$	73.262	69.814	70.675	70.904
(45) $C_2H_3^{\bullet}\cdots Cl^-$	74.942	70.137	71.325	71.614

[a] 6-311++G(2d,2p) basis set used. [b] aug-cc-pVTZ basis set used. [c] Stable *σ** structure not found. [d] Stable *π** structure not found.

anions they were 5.78, 4.85, and 5.12 kcal/mol for the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), and B3LYP/6-311++G(2d,2p) methods, respectively. The isodesmic estimates for the $-H\cdots Cl^-$ radical anions are much more sensitive to the level of theory. Large differences are found between the LDA and RCCSD(T) levels, whereas fairly small differences are seen between the B3LYP/6-311++G(2d,2p) and RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) levels. The worst case difference is for *trans*-$C_2HCl_2^{\bullet}\cdots Cl^-$ (34), with a difference of 9 kcal/mol between the LDA/6-311++G(2d,2p) and RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) levels, respectively. The average absolute differences from the RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) isodesmic data were 5.95, 3.64, and 1.18 kcal/mol for the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), and B3LYP/6-311++G(2d,2p) methods, respectively. Although the differences are fairly large for the $-H\cdots Cl^-$ radical anions, the differences appear to be systematic, with the values increasing sequentially from the right side to the left side of the table (i.e., LDA < PBE96 < B3LYP < RCCSD(T)).

For the "loose" *σ** and $-H\cdots Cl^-$ radical anion complexes, the calculated stability is subject to possible basis set superposition error, and this is most important when the binding energy is small. We calculated the basis set superposition error for two representative cases $C_2Cl_3^{\bullet}\cdots Cl^-$ and $CCl_2CH^{\bullet}\cdots Cl^-$ and observed that in both cases the bond dissociation energy to the (radical + Cl^-) products was decreased by less than 0.5 kcal/mol (0.45 and 0.29 kcal/mol, respectively, at the B3LYP/6-311++G(2d,2p) level). Thus the BSSE is likely to be small for any of the systems for which it may come into play in this study. We note further that our ultimate interest is for aqueous conditions where the "loose" complexes likely do not exist owing to the stronger solvation of an isolated chloride ion over the complexes; therefore we decided to report only the non-BSSE corrected data. We believe that our conclusions would not be affected by (small) BSSE corrections.

The calculated values of *S*° at 298.15 K for the gas-phase radical anions are given in Table 5, and a table of calculated ΔG_f°'s at 298 K is given as Supporting Information. Reported entropy estimates for the radical anions are not expected to be as accurate for the neutral compounds, because many of them are loosely bound molecules and their vibrational motion is not well described by harmonic normal vibrations. As expected, fairly large variations are seen in the calculated entropies. Estimating accurate entropies in this situation can be a computationally very demanding task, requiring account of anharmonicities. However, given the difficulty associated with calculating the partition function including full anharmonicity, these are the best available.

The free energies of solvation calculated using SCRF theory at various electronic structure levels for the radical anions are given Table 6. These calculations were performed by using the optimized gas-phase geometries at the specific computational level. The average absolute differences from COSMO LDA/6-311++G(2d,2p) calculations are 1.1 and 2.9 kcal/mol, respec-

TABLE 6: SCRF Calculated Free Energies of Solvation (kcal/mol)[a]

	ΔG_{SCRF}		
	LDA[b]	PBE96[b]	B3LYP[b]
σ* Structures			
(23) $C_2Cl_3\cdots Cl^-$	−44.44	−45.85	−46.97
(24) *trans*-$C_2HCl_2\cdots Cl^-$	−58.34	−58.56	−60.02
(25) *cis*-$C_2HCl_2\cdots Cl^-$	−49.18	−49.24	−50.40
(26) 1,1-$C_2HCl_2\cdots Cl^-$	−45.98	−45.74	−48.75
(27) *trans*-$C_2H_2Cl\cdots Cl^-$	−47.02	*c*	*c*
(28) *cis*-$C_2H_2Cl\cdots Cl^-$	−53.14	−54.69	−57.58
(29) 1,1-$C_2H_2Cl\cdots Cl^-$	−53.41	−53.82	−55.02
$C_2H_3\cdots Cl^-$	*c*	*c*	*c*
π* Structures			
(30) $C_2Cl_4^-$	−42.93	−42.07	−42.12
(31) $C_2HCl_3^-$	−47.86[e]	−47.33[e]	−47.37[e]
(32) *trans*-$C_2H_2Cl_2^-$	−53.88[e]	−53.20[e]	−53.16[e]
(33) *cis*-$C_2H_2Cl_2^-$	*d*	*d*	*d*
1,1-$C_2H_2Cl_2^-$	*d*	*d*	*d*
$C_2H_4^-$	*d*	*d*	*d*
−H−Cl⁻ Structures			
(34) *trans*-$C_2HCl_2{}^\bullet\cdots Cl^-$	−48.67	−49.79	−52.97
(35) *cis*-$C_2HCl_2{}^\bullet\cdots Cl^-$	−51.41	−52.95	−55.31
(36) 1,1-$C_2HCl_2{}^\bullet\cdots Cl^-$	−48.31	−49.26	−49.22
(37) *trans*-$C_2H_2Cl^\bullet\cdots$*cis*-Cl^-	−53.34	−54.28	−56.24
(38) *trans*-$C_2H_2Cl^\bullet\cdots$iso-Cl^-	−54.10	−55.90	−58.43
(39) *cis*-$C_2H_2Cl^\bullet\cdots$*trans*-Cl^-	−51.79	−53.01	−55.39
(40) *cis*-$C_2H_2Cl^\bullet\cdots$iso-Cl^-	−51.62	−53.23	−56.39
(41) 1,1-$C_2H_2Cl^\bullet\cdots$*cis*-Cl^-	−52.48	−53.62	−56.89
(42) 1,1-$C_2H_2Cl^\bullet\cdots$*trans*-Cl^-	−54.55	−56.29	−58.42
(43) $C_2H_3{}^\bullet\cdots Cl^-$	−58.01	−59.48	−61.19
(44) $C_2H_3{}^\bullet\cdots Cl^-$	−56.30	−58.19	−60.96
(45) $C_2H_3{}^\bullet\cdots Cl^-$	−59.06	−61.03	−63.09

[a] 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. [b] 6-311++G(2d,2p) basis set used. [c] Stable σ* structure not found. [d] Stable π* structure not found. [e] ROHF geometry used.

tively, for COSMO PBE96/6-311++G(2d,2p) and COSMO B3LYP/6-311++G(2d,2p).

V. Reaction Energies

With all of the calculated values described above, energetics of possible pathways of the first one-electron reduction of chloroethylenes were estimated. The results shown in Table 7 were based on the values obtained from Tables 1 and 2 for $\Delta H_f^\circ(C_2H_xCl_{3-x}{}^\bullet{}_{(g)})$, $\Delta H_f^\circ(C_2H_xCl_{3-x}{}^-{}_{(g)})$, and $\Delta H_f^\circ(C_2H_xCl_{4-x}{}^-{}_{(g)})$. The remaining values needed to generate Table 5 can be found in Table A1, which contains experimental and high quality ab initio values for $\Delta H_f^\circ(Cl^-{}_{(g)})$, $\Delta H_f^\circ(Cl^\bullet{}_{(g)})$, $\Delta H_f^\circ(C_2H_xCl_{4-x(g)})$, and $\Delta H_f^\circ(e^-{}_{(g)})$. There was reasonable agreement between reaction energies of the different ab initio levels. The average absolute differences from the RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) isodesmic were 2.9, 2.2, and 1.4 kcal/mol for the LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), and B3LYP/6-311++G(2d,2p) methods, respectively, and the largest absolute difference was 7.3 kcal/mol between the SVWN5/6-311++G(2d,2p) and RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(2d,2) reaction energies of the reaction ($C_2HCl_3 + 1e^- \rightarrow$ *trans*-$C_2HCl_2{}^\bullet\cdots Cl^-$).

For the gas-phase reduction of $C_2Cl_4^-$, the most favorable pathway is sensitive to the level of theory. RCCSD(T) calculations predict the formation of the σ* radical anion to be the lowest energy pathway. However, the second most stable pathway, which resulted in the formation of the π* radical anion, was nearly isoenergetic with the first pathway (∼3 kcal/mol higher in energy). DFT calculations on the other hand predicted that the π* radical anion would be favored over the σ* radical anion by ∼4 kcal/mol. The reaction yielding $C_2HCl_3{}^\bullet$ and Cl^- was 8−12 kcal/mol less favorable, and the formation of $C_2HCl_3^-$ and $Cl^\bullet$ was found to be most unfavorable. For the reduction of C_2HCl_3, *trans*-$C_2H_2Cl_2$, *cis*-$C_2H_2Cl_2$, and 1,1-$C_2H_2Cl_2$, the formation of the π* radical anion was not the lowest energy pathway. Instead, the thermodynamically most favorable reactions yielded a radical anion complex with the chloride ion bonded to a hydrogen atom $-H\cdots Cl^-$ or possibly the σ* radical anion in some cases. The formation of a σ* radical anion was nearly isoenergetic for the reduction of C_2HCl_3 and *trans*-$C_2H_2Cl_2$. Reductions yielding $C_2H_xCl_{3-x}{}^\bullet$ and Cl^- were again found to be considerably less favorable, and the formation of $C_2H_xCl_{3-x}{}^-$ $Cl^\bullet$ was found to be most favorable.

TABLE 7: Gas-Phase Enthalpies of Reaction (kcal/mol)

reactants	products	LDA	PBE96	B3LYP	RCCSD(T)
Radical + Chloride Ion Reactions					
$C_2Cl_4 + e^-$	(8) + Cl^-	0.25	−0.26	0.25	2.33
$C_2HCl_3 + e^-$	(9) + Cl^-	6.94	6.96	7.51	8.63
	(10) + Cl^-	6.39	5.94	6.43	7.94
	(11) + Cl^-	11.17	10.33	10.25	11.39
trans-$C_2H_2Cl_2 + e^-$	(12) + Cl^-	11.44	10.59	10.39	11.10
cis-$C_2H_2Cl_2 + e^-$	(13) + Cl^-	11.90	11.30	11.14	11.56
1,1-$C_2H_2Cl_2 + e^-$	(14) + Cl^-	6.17	6.37	7.06	7.77
Anion + Chlorine Atom Reactions					
$C_2Cl_4 + e^-$	(16) + $Cl^\bullet$	27.78	26.14	24.91	26.99
$C_2HCl_3 + e^-$	(17) + $Cl^\bullet$	42.92	41.46	39.29	40.76
	(18) + $Cl^\bullet$	41.09	38.97	38.12	40.63
	(19) + $Cl^\bullet$	44.46	*a*	*a*	*a*
trans-$C_2H_2Cl_2 + e^-$	(20) + $Cl^\bullet$	*a*	*a*	*a*	*a*
cis-$C_2H_2Cl_2 + e^-$	(21) + $Cl^\bullet$	*a*	*a*	*a*	*a*
1,1-$C_2H_2Cl_2 + e^-$	(22) + $Cl^\bullet$	55.42	53.83	51.91	53.32
σ* Radical Anion Reactions					
$C_2Cl_4 + e^-$	(23)	−8.46	−7.36	−7.42	−8.77
$C_2HCl_3 + e^-$	(24)	0.13	0.59	0.59	−1.85
	(25)	−4.51	−4.39	−4.49	−5.85
	(26)	*a*	*a*	1.08	0.37
trans-$C_2H_2Cl_2 + e^-$	(27)	−3.74	−3.24	−2.03	−1.10
cis-$C_2H_2Cl_2 + e^-$	(28)	9.39	10.36	10.76	8.77
1,1-$C_2H_2Cl_2 + e^-$	(29)	5.11	5.45	5.07	2.19
π* Radical Anion Reactions					
$C_2Cl_4 + e^-$	(30)	−12.28	−11.69	−11.91	−5.48
$C_2HCl_3 + e^-$	(31)	−0.41	0.34	0.27	5.67
trans-$C_2H_2Cl_2 + e^-$	(32)	13.40	14.85	14.33	17.85
$-H\cdots Cl^-$ Radical Anion Reactions					
$C_2HCl_3 + e^-$	(34)	−15.04	−11.91	−7.70	−7.70
	(35)	−11.73	−9.47	−6.61	−6.61
	(36)	−11.00	−9.26	−7.01	−7.01
trans-$C_2H_2Cl_2 + e^-$	(37)	−6.68	−5.27	−3.55	−3.55
	(38)	−5.53	−3.16	−0.83	−0.83
cis-$C_2H_2Cl_2 + e^-$	(39)	−7.63	−5.84	−3.92	−3.92
	(40)	−7.90	−4.94	−1.93	−1.93
1,1-$C_2H_2Cl_2 + e^-$	(41)	−10.02	−7.30	−3.59	−3.59
	(42)	−7.01	−4.68	−2.26	−2.26

[a] Stable structure not found.

In addition, Table 7 shows that the reduction of the compounds considered in this study are strongly dependent on the degree of chlorination. For the radical + chloride ion reactions, C_2Cl_4 with four chlorine atoms is, on average, 11 kcal/mol more energetically favorable to reduce than chloroethylenes with only two chlorine atoms. Similar dependencies on the degree of chlorination are seen for the other reactions. 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.,[52] chlorine substitutions appear to have an almost exclusively steric effect and, in

TABLE 8: Aqueous-Phase Heats of Reaction (kcal/mol)

reactants	products	LDA	PBE96	B3LYP
Radical + Chloride Ion Reactions				
$C_2Cl_4 + e^-$	(8) + Cl^-	−47.16	−47.54	−46.97
$C_2HCl_3 + e^-$	(9) + Cl^-	−41.39	−41.20	−40.57
	(10) + Cl^-	−41.66	−41.96	−41.38
	(11) + Cl^-	−36.17	−36.86	−36.88
trans-$C_2H_2Cl_2 + e^-$	(12) + Cl^-	−37.29	−37.98	−38.10
cis-$C_2H_2Cl_2 + e^-$	(13) + Cl^-	−37.32	−37.69	−37.76
1,1-$C_2H_2Cl_2 + e^-$	(14) + Cl^-	−42.20	−41.89	−41.08
Anion + Chlorine Atom Reactions				
$C_2Cl_4 + e^-$	(16) + $Cl^\bullet$	3.19	2.19	0.59
$C_2HCl_3 + e^-$	(17) + $Cl^\bullet$	14.28	13.39	11.37
	(18) + $Cl^\bullet$	12.97	11.11	10.60
	(19) + $Cl^\bullet$	19.20	*a*	*a*
trans-$C_2H_2Cl_2 + e^-$	(20) + $Cl^\bullet$	*a*	*a*	*a*
cis-$C_2H_2Cl_2 + e^-$	(21) + $Cl^\bullet$	*a*	*a*	*a*
1,1-$C_2H_2Cl_2 + e^-$	(22) + $Cl^\bullet$	20.82	19.80	17.69
σ^* Radical Anion Reactions				
$C_2Cl_4 + e^-$	(23)	−24.93	−26.82	−26.84
$C_2HCl_3 + e^-$	(24)	−28.98	−29.23	−30.98
	(25)	−26.11	−25.60	−26.46
	(26)	*a*	*a*	−19.45
trans-$C_2H_2Cl_2 + e^-$	(27)	−22.15	−21.44	−20.68
cis-$C_2H_2Cl_2 + e^-$	(28)	−14.59	−15.61	−18.60
1,1-$C_2H_2Cl_2 + e^-$	(29)	−21.00	−21.05	−22.36
π^* Radical Anion Reactions				
$C_2Cl_4 + e^-$	(30)	−26.65	−25.35	−25.34
$C_2HCl_3 + e^-$	(31)	−18.30	−17.02	−17.13
trans-$C_2H_2Cl_2 + e^-$	(32)	−10.11	−7.98	−8.47
$-H\cdots Cl^-$ Radical Anion Reactions				
$C_2HCl_3 + e^-$	(34)	−31.12	−30.50	−28.11
	(35)	−35.32	−33.50	−32.31
	(36)	−34.86	−34.45	−33.79
trans-$C_2H_2Cl_2 + e^-$	(37)	−31.68	−31.35	−31.55
	(38)	−31.09	−30.67	−30.87
cis-$C_2H_2Cl_2 + e^-$	(39)	−31.11	−30.65	−31.11
	(40)	−30.83	−29.62	−29.84
1,1-$C_2H_2Cl_2 + e^-$	(41)	−34.97	−33.59	−33.08
	(42)	−34.10	−33.79	−33.45

[a] Stable structure not found.

fact, the C−Cl bonds get weaker as the number of chlorines increases. In contrast, for fluorcarbons increased fluorination results in an increasing C−F bond strength.

The aqueous phase reaction free energies are given in Table 8 and allow us to investigate the role of solvation. Table 8 was generated by using experimental and high quality ab initio values for $\Delta G_f^\circ(Cl^-_{(aq)})$, $\Delta G_f^\circ(Cl^\bullet_{(aq)})$, $\Delta G_f^\circ(C_2H_xCl_{4-x(aq)})$, and $\Delta G_f^\circ(e^-_{(aq)})$ found in Table A2 and the remaining values, $\Delta H_f^\circ(C_2H_xCl_{3-x}{}^\bullet{}_{(g)})$, $\Delta H_f^\circ(C_2H_xCl_{3-x}{}^-{}_{(g)})$, $\Delta H_f^\circ(C_2H_xCl_{4-x}{}^-{}_{(g)})$, $S^\circ(C_2H_xCl_{3-x}{}^\bullet{}_{(g)})$, $S^\circ(C_2H_xCl_{3-x}{}^-{}_{(g)})$, $S^\circ(C_2H_xCl_{4-x}{}^-{}_{(g)})$, $\Delta G_s(C_2H_xCl_{3-x}{}^\bullet{}_{(g)})$, $\Delta G_s(C_2H_xCl_{3-x}{}^-{}_{(g)})$, and $\Delta G_s(C_2H_xCl_{4-x}{}^-{}_{(g)})$ were obtained from Tables 1−6. Solvation significantly changed which reactions were most favorable. In all cases, the thermodynamically most favorable reactions were the radical + chloride ion reactions. The reason for the dramatic change in reaction energetics is that the solvation of Cl^- is much stronger than that of the radical anions (e.g., $\Delta G_s(Cl^-) = -75$ kcal/mol, ΔG_s(*trans*-$C_2HCl_2{}^\bullet\cdots Cl^-) = -53$ kcal/mol). The next most favorable reactions are the $-H\cdots Cl^-$ radical anion reactions, followed by the σ^* and π^* radical anion reactions. Finally, the high energy anion + chlorine atom reactions are still predicted to be unfavorable pathways when the effect of solvent is included.

VI. Conclusion

Ab initio electronic structure theory, canonical ensemble entropy formulas, and self-consistent reaction field theory were used to estimate the thermochemical properties, ΔH_f°(298.15 K), S°(298.15 K,1 bar), and ΔG_S(298.15 K, 1bar), of 37 different polychloroethylenyl radicals, anions, and radical anion complexes: $C_2H_yCl_{3-y}{}^\bullet$, and $C_2H_yCl_{3-y}{}^-$, and $C_2H_yCl_{4-y}{}^{\bullet-}$ for $y = 0-3$. The most difficult computational step in our thermodynamic estimations was determining the gas-phase enthalpies of formation, ΔH_f°(298.15 K). A strategy based on isodesmic reactions was used to reduce the error associated with determining ΔH_f°(298.15 K). This strategy was found be quite reliable for determining the gas-phase enthalpies of formation for the polychloroethylenyl radicals and ions. For the radical anion complexes, the isodesmic estimations were found to much more sensitive to the level of theory. The isodesmic estimates were especially sensititve for the $-H\cdots Cl^-$ radical anions. The worst case difference was for *trans*-$C_2HCl_2{}^\bullet\cdots Cl^-$ (34), where a difference of 9 kcal/mol was seen between the LDA/6-311++G-(2d,2p) and RCCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G-(2d,2p) levels. Our results did not suggest a best lower-level ab initio method for the entire set of compounds studied. The LDA/6-311++G(2d,2p) results seemed the most reliable for the polychloroethylenyl radicals and σ^* radical anions, whereas B3LYP/6-311++G(2d,2p) results seem to work the best for the polychloroethylenyl anions and $-H\cdots Cl^-$ radical anions.

The calculated thermochemical properties allowed us to estimate the energetics of several one-electron reductive pathways. 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 polychlorinated ethylenes were predicted. In almost all of the gas-phase reactions, the thermodynamically most favorable pathways resulted in a $C_2H_yCl_{4-y}{}^{\bullet-}$ $-H\cdots Cl^-$ radical anion complex. The exception was for the reduction of C_2Cl_4, in which the most favorable pathway yielded a σ^* radical anion, or possibly the nearly isoenergetic π^* radical anion. Solvation significantly changed the products. The thermodynamically most favorable pathway in the aqueous phase always resulted in a chloride dissociation products $C_2H_yCl_{3-y}{}^\bullet$ and Cl^-. In addition, the results of this study indicated that a higher degree of chlorination corresponds to a more favorable reduction. This trend, previously explained by Kumaran et al.,[52] 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.

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

compd	ΔH_f°	compd	ΔH_f°
H_2	0.0	*trans*-$C_2H_2Cl_2$	0.4[a]
e^-	0.0[b]	*cis*-$C_2H_2Cl_2$	1.0[a]
$H^\bullet$	52.1[b]	1,1-$C_2H_2Cl_2$	0.5[a]
$C^\bullet$	171.3[b]	C_2H_3Cl	7.0[a]
$Cl^\bullet$	29.1[b]	C_2H_4	12.5[a]
Cl^-	−55.9[a]	C_2H_3	71.0[a]
C_2Cl_4	−3.0[a]	$C_2H_3{}^-$	56.2[a]
C_2HCl_3	−4.6[a]		

[a] Experimental ref 58. [b] Experimental ref 56.

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

compd	ΔG°_f(298.15 K,aq)
e^-	64.0[a,b]
H^+	0.0
Cl^-	−31.4[c]

[a] $\Delta G_s(e^-) = -34.6$ kcal/mol from refs 59 and 60. [b] $E^\circ_H = 98.6$ kcal/mol calculated from $\Delta G_s(H^+) = -263.98$ kcal/mo[60] and $\Delta G^\circ_f(H^+_{(g)}) = 362.58$ kcal/mol.[56] [c] ΔG°_f(aq) obtained experimental ref 56.

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Supporting Information Available: Tables of ab initio total energies and enthalpy corrections for all compounds in this study, from LDA/6-311++G(2d,2p), PBE96/6-311++G(2d,2p), B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and RCCSD(T)/aug-cc-pVTZ total energy and vibrational calculations. In addition, the optimized structures for all the molecules calculated can be obtained by correspondence with E.J.B. (Eric.Bylaska@pnl.gov).

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