Reductive Dechlorination of Hexachloroethane in the Environment: Mechanistic Studies via Computational Electrochemistry

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Abstract: Ab initio and density functional levels of electronic structure theory are applied to characterize alternative mechanisms for the reductive dechlorination of hexachloroethane (HCA) to perchloroethylene (PCE). Aqueous solvation effects are included using the SM5.42R continuum solvation model. After correction for a small systematic error in the electron affinity of the chlorine atom, theoretical predictions are accurate to within 23 mV for four aqueous reduction potentials relevant to HCA. A single pathway that proceeds via two successive single-electron transfer/barrierless chloride elimination steps, is predicted to be the dominant mechanism for reductive dechlorination. An alternative pathway predicted to be accessible involves trichloromethylchlorocarbene as a reactive intermediate. Bimolecular reactions of the carbene with other species at millimolar or higher concentrations are predicted to potentially be competitive with its unimolecular rearrangement to form PCE.

Introduction

Small, polychlorinated organic compounds such as hexachloroethane (HCA) are widespread trace-level contaminants in drinking water supplies.[1−4] As many of these species are known or suspected human carcinogens, considerable effort has gone into the development of technologies for the in situ transformation of these environmental contaminants to less dangerous products. One such method is reductive dehalogenation via zero-valent iron,[5] where oxidation of Fe^0 to Fe(II) drives the reduction of halogenated hydrocarbons in aqueous solutions that are in contact with the metal.[6−8]

Several recent papers have reported zero-valent metal-mediated reductive dechlorination of substituted methanes,[9,10] larger alkanes,[7] and ethylenes.[11,12] In the case of HCA, the use of sulfidic[6,8,13−15] and other[16] reducing agents has also been extensively examined. In addition, decomposition of chlorinated hydrocarbons with alternative sources of reducing power (e.g., TiO_2/UV, alternative electrochemical couples, autotrophic enzyme activity) have been reported.[7,17,18] Most of these reports have focused on how reaction conditions affect the kinetics of disappearance of HCA, with some additional analysis of product distributions.

A number of possible pathways have been suggested for the zero-valent iron reductive elimination of chlorine from hexachloroethane. These are summarized in Chart 1. All share in common the observation that perchloroethylene (PCE) is the major product of reductive dehalogenation of HCA. Butler and Hayes[6] have observed small amounts (no more than 1% of initial HCA concentration) of pentachloroethane (PCA) as an intermediate when sulfide is used as a reductant; transformation of PCA to PCE by dehydrohalogenation in aqueous systems has been previously studied.[19] As accurate thermochemical data are not available for many of the reactive intermediates in pathways (a−d), the mechanism is not firmly established.

We present here high-level quantum chemical calculations having the goal of accurately describing the thermochemistry for different possible microscopic steps in the reductive dechlorination pathway. Electron correlation is included by coupled-cluster theory and density functional theory (DFT). The effects of aqueous solvation are included in the quantum mechanical treatment using the SM5.42R continuum model.[20] We first validate the computational models for polychlorinated species

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Chart 1

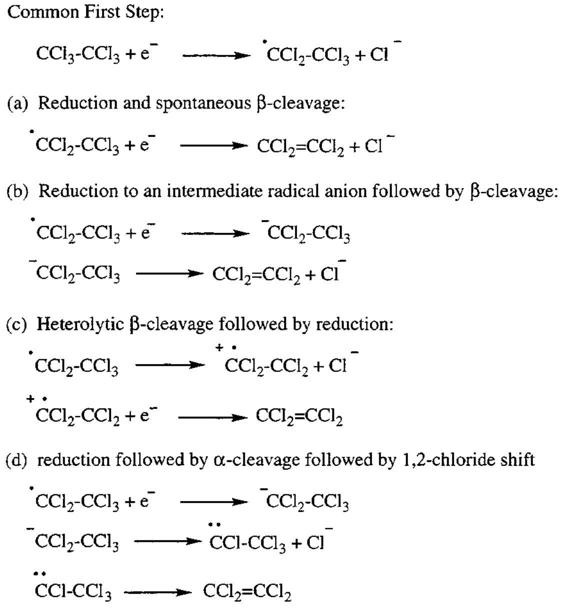

Table 1. Standard-State Values of Gas-Phase Absolute Entropies and Free Energies of Solvation for HCA and Some Products of Its Reductive Dechlorination

	S°_{298}, J mol^{-1} K^{-1}		$\Delta G^{*}_{\text{hyd}}$, kJ mol^{-1}	
molecule	expt^{a}	calcd^{b}	expt	calcd^{c}
HCA	397.8	394.5	−5.9^{d}	−3.6
PCA	380.6^{e}	387.4	−5.7^{d}	−6.0
PCE	343.4	363.8	0.2^{d}	1.5
H^+	109.0	109.0	−1103^{f}	−1103^{g}
$Cl^{\bullet}$	165.2	164.9		−1.0
Cl^-	153.4	153.4	−322.2^{h}	−323.0

[a] Data in this column are from ref 37 unless otherwise specified. [b] BPW91/aug-cc-pVDZ. [c] SM5.42R/BPW91/DZVP//BPW91/aug-cc-pVDZ. [d] Reference 41. [e] Reference 39. [f] Reference 40. [g] The SM5.42R model is not designed for calculations on the bare proton, and therefore we use the experimental value of $\Delta G^{*}_{\text{hyd}}(H^+)$ in all SM5.42R calculations in this paper. [h] Reference 38.

and their reduction products by comparison to relevant thermochemical data both in the gas phase and in aqueous solution, and we then apply them to the characterization of reaction paths (a−d) in Chart 1.

Computational Methods

The absolute standard-state free energy for molecule X, $G^{\circ}(X_{(g)})$, is the sum of the nuclear repulsion energy, Born−Oppenheimer electronic ground-state energy, zero-point vibrational energy, and electronic, vibrational, rotational, and standard-state translational thermal contributions (computed, assuming ideal gas behavior for a rigid rotor with all vibrations treated as harmonic oscillators and the electronic partition function equal to the ground-state degeneracy except for Cl atom where the $^{2}P_{1/2}$ excited state is also included). In this paper, the standard state for gas-phase species is an ideal gas at a temperature of 298 K and a pressure of 1 bar (0.987 atm).

To compute absolute free energies, different levels of electronic structure theory were employed. All molecular geometries were optimized in the gas phase using the gradient-corrected density functionals of Becke[21] for exchange and of Perdew and Wang[22] for correlation with the aug-cc-pVDZ basis set;[23−25] we will follow the usual convention of referring to this combination of density functionals as BPW91. Analytic frequency calculations were carried out to verify the nature of all stationary points (minima or transition states) and to calculate zero-point vibrational energies and thermal contributions to the enthalpy and free energy at 298 K. Single-point calculations at the BPW91 geometries were also carried out accounting for electron correlation with unrestricted coupled-cluster theory including all single and double excitations with fourth and fifth order triple excitations estimated quasiperturbatively (CCSD(T))[26−28] using the aug-cc-pVDZ basis set.

Standard state solvation free energies in water (dielectric constant $\epsilon = 78.3$[29]) were calculated using the SM5.42R/BPW91/DZVP aqueous model[20] based on empirical atomic surface tensions and self-consistent reaction field calculations with CM2 class IV charges[30] obtained with the DZVP basis set;[31] these calculations employed the gas-phase BPW91/aug-cc-pVDZ geometries (the R in SM5.42R denotes that the model was employed by using gas-phase geometries kept rigid in the liquid solution phase, and that the parametrization includes the effects of liquid-state geometry relaxation implicitly). We will refer to this level hereafter simply as SM5.42R. All calculations were carried out with a locally modified version of the Gaussian 98 electronic structure program suite.[32,33]

Because standard-state conventions differ for electrolytes and nonelectrolytes in solution, care must be taken to ensure appropriate comparisons between theory and experiment. The appendix addresses standard-state issues in detail.

Results and Discussion

Computational Validation. The theoretical models used here have been broadly validated for a wide range of chemical functionality.[34−36] Prior to using them to analyze individual steps in the reductive dechlorination of HCA, to add confidence in their application to this specific kind of problem, we evaluate the utility of the employed theoretical levels for reactions involving HCA and products of its reductive dechlorination. In many instances absolute entropies and free energies of solvation, both of which permit direct comparison between theory and experiment, are available[37−41] for these molecules; these data are provided in Table 1. Calculated gas-phase absolute entropies S°_{298} and standard-state free energies of aqueous solvation

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Table 2. Experimental and Theoretical Thermochemistry of Processes Relevant to Reductive Dechlorination of HCA[a]

process	phase	thermochemical quantity	expt	CCSD(T)[b]	BPW91[b]
(A) $PCE \rightarrow PCE^{+\bullet} + e^-$	gas	ΔH_0 (IP)	9.33[c] (9.5)[d,e]	9.18 (9.42)[d]	8.81 (9.02)[d]
(B) $Cl^\bullet + e^- \rightarrow Cl^-$	gas	$-\Delta H_0$ (EA)	3.61[f]	3.40	3.64
	aqueous	$E_1^{\phi'}$	2.54	2.29	2.54
(C) $HCA + 2e^- + H^+ \rightarrow PCA + Cl^-$	gas	$\Delta G^o_{(g)}$	−18.54	−18.28	−18.55
	aqueous	$E_1^{\phi'}$	0.67	0.55	0.69
(D) $HCA + 2e^- \rightarrow PCE + 2Cl^-$	gas	$\Delta G^o_{(g)}$	−4.37	−3.90	−4.61
	aqueous	$E_2^{\phi'}$	1.15	0.93	1.28
(E) $HCA + e^- \rightarrow PCA^\bullet + Cl^-$	gas	$\Delta G^o_{(g)}$	−1.16	−0.96	−1.45
	aqueous	$E_1^{\phi'}$	0.11	−0.06	0.44

[a] Computed from data in Tables 1, S-1, and S-2 unless otherwise indicated; reduction potentials in V, all other thermochemical quantities in eV. [b] Includes SM5.42R solvation free energies for predicted reduction potentials in aqueous solution. [c] Reference 42. [d] Values in parentheses are for vertical process. [e] Reference 43. [f] Reference 44.

$\Delta G^*_{\mathrm{hyd}}$ are from the BPW91 and SM5.42R levels of theory, respectively. The average agreement between theory and experiment for absolute entropies in Table 1 is better than 3%, and for solvation free energies the average absolute deviation of theory from experiment is 1.2 kJ mol^{-1} (excluding H$^+$).

For five processes (labeled (A−E)), Table 2 presents a comparison of experimental and computed free energies of reaction and enthalpies of ionization that can be derived from the data in Table 1 and additional data provided in Tables S-1 and S-2 of the Supporting Information. Table S-1 contains all of the electronic and zero-point vibrational energies, thermal corrections, and free energies of solvation from the theoretical calculations. Table S-2 contains experimental heats of formation, entropies, free energies of formation, and solvation free energies that are available.[42−44]

Focusing first on comparisons of gas-phase data, we see from Table 2 that the CCSD(T) level is fairly accurate for the ionization processes (A) and (B), with an average absolute error of 0.15 eV over the two adiabatic and one vertical process. The largest error, 0.21 eV, is for the electron affinity (EA) of the chlorine atom. For the same EA, DFT is within 0.03 eV of experiment. DFT is less accurate for the adiabatic and vertical ionization potentials (IPs) of PCE, underestimating those potentials by about 0.5 eV. DFT is known to predict anomalous stabilities for radicals and ions that can be highly delocalized,[45−48] and this is consistent with the nature of the π system in PCE$^{+\bullet}$ and the underestimation of these IPs. For the gas-phase electrochemical half-reactions (C), (D), and (E), CCSD(T) consistently underestimates the exergonicity. The underestimation averages about 0.23 eV per chloride ion produced, suggesting that most of the error is associated with CCSD(T) underestimating the EA of the chlorine atom. Indeed, if one applies an after-the-fact correction of −0.23 eV per chloride ion produced to the CCSD(T) predictions, they are on average within 0.02 eV of experiment. It should be noted that the "experimental" free energy of formation for PCA$^\bullet$ is derived from a heat of formation having an 8 kJ mol^{-1} uncertainty and a theoretical absolute entropy (no experimental entropy has been measured)—the reasonable agreement between the "corrected" CCSD(T) prediction and the experimental value suggests, however, that the latter is reasonable.

DFT shows very good predictive utility for reaction (C) but overestimates the exergonicity of reactions (D) and (E) by 0.24 and 0.29 eV, respectively. Again, this is consistent with DFT's tendency to overstabilize delocalized systems; in reaction (D) product PCE has a closed-shell π system where reactant HCA does not, and in reaction (E) product PCA$^\bullet$ can achieve a high degree of hyperconjugative stabilization of the σ radical.

Table 2 also compares theory to experiment for one- and two-electron reduction potentials ($E_1^{\phi'}$ and $E_2^{\phi'}$, respectively) associated with reductive dechlorination of HCA in aqueous solution. These are computed from the Nernst equation

$$E_n^{\phi'} = -\Delta G_{(\mathrm{aq})}^{\phi'}/nF \qquad (1)$$

where $\Delta G_{(\mathrm{aq})}^{\phi'}$ is the free energy change for a half-reaction, n is the number of electrons consumed by the reduction, F is Faraday's constant (96.485 kJ V^{-1} mol^{-1}), and all relevant standard state conventions are detailed in the Appendix. We note that, using the data in Tables 1, S-1, and S-2, we calculate experimental $E_2^{\phi'}$ values for reactions (C) and (D) within 20 mV of those reported by previous workers [49−51] following a similar protocol but with sometimes older sources of thermochemical data. For reaction (E), Totten and Roberts [51] have identified errors in previous derivations from use of incorrect entropies of formation for some species, and their more recent derivation is $E_1^{\phi'} = 0.15$ V. That number is only partially based on experimental data, since it was derived assuming the free energy of solvation for PCA$^\bullet$, which is not known experimentally, to be equal to the free energy of solvation for PCA (Table 1). We have chosen to use a value for the free energy of solvation of PCA$^\bullet$ that is 4.8 kJ mol^{-1} smaller than that for PCA because that is the difference in the SM5.42R solvation free energies calculated for the two molecules, and this accounts for the 40 mV difference between our best estimate value and that derived by Totten and Roberts.[51]

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For all four aqueous reductions, CCSD(T) continues to show a consistent error associated with the number of chloride ions produced. In this case, if a correction is applied of

$$Z = 0.22m/n \text{ V} \qquad (2)$$

where m is the number of chloride ions produced, and n is the number of electrons consumed by the reduction, then CCSD(T) + Z has an average unsigned error over all four reductions of 23 mV. Note that, except for scaling by $-1/n$ because of eq 1, the error in the CCSD(T) method in aqueous solution is almost exactly that found in the gas phase and attributed to the underestimation of the chlorine atom EA. This suggests that the SM5.42R model accurately predicts changes in solvation free energies on going from reactants to products in all of the different processes. Moreover, the largest error, 50 mV, is associated with reaction (E), where the experimental uncertainty is greatest as noted above.

Note that the correction of eq 2 would not be necessary if we used the best experimental value instead of the calculated electron affinity for Cl; in general for applications to practical problems, use of experimental values where known may lead to more accurate models, although good judgment should be exercised when mixing theory and experiment.

Given that the solvation free energy changes are modeled accurately by SM5.42R, DFT should do about as well in predicting aqueous solution reduction potentials as it does for predicting gas-phase exergonicities, and that proves to be the case. DFT is very accurate for reaction (C) but overestimates the reduction potentials of reactions (D) and (E), in the latter instance by 0.33 V.

The success of the CCSD(T) method (especially after application of empirical corrections, or alternatively after improving the basis set to correct for a systematic underestimation of the chlorine atom EA) bodes well for future applications to predict the reduction potentials of other chlorinated aliphatics and, by extension, other environmental contaminants as well. Such reduction potentials have been shown to be useful predictors of reduction rate constants in zero-valent metal-mediated reductions.[52,53] DFT, which is less computationally intensive, may be a useful predictive alternative for reductions where neither reactants nor products are handled anomalously by the method (vide supra). For the remainder of the present paper, however, the robustness of the CCSD(T) approach allows us to proceed with an analysis of the microscopic steps involved in reductive dechlorination with confidence in the quantitative accuracy of the results.

Mechanism of Reductive Dechlorination. The various possible steps in the reductive dechlorination of HCA are detailed in Figure 1, with ball-and-stick structures of the molecular geometries for the various intermediates provided. For equilibrated species, each structure is accompanied by our best estimates (CCSD(T) + SM5.42R, and with the −0.23 eV correction for free chloride ions) of the gas-phase and aqueous free energies in eV. To facilitate comparisons the standard-state convention is that all free energies, both gas-phase and in aqueous solution, are ΔG^{o} values (i.e., the identical convention is used for electrolytes and nonelectrolytes in aqueous solution, which is not true for the convention used for ΔG^{ϕ} values, where the ΔG^{ϕ} notation is explained in the Appendix). The figure also includes some nascent anions produced by vertical electron attachment. The energy associated with such a species in the gas phase is the free energy of the precursor neutral adjusted by the change in Born−Oppenheimer ground-state electronic energy upon attachment; in aqueous solution, this is further adjusted by the change in equilibrium free energy of solvation, which is used as an approximation to the nonequilibrium solvation energy[54] of the nascent vertical species.

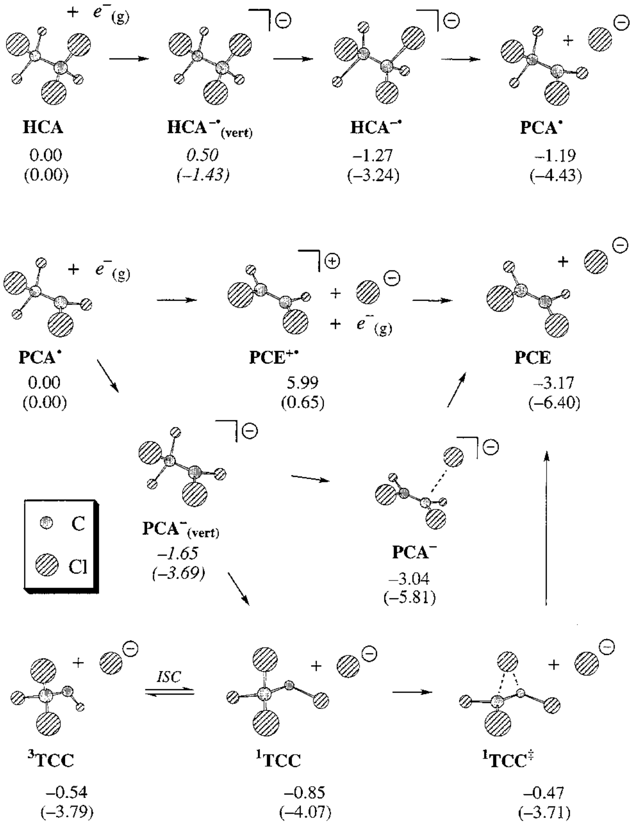

Figure 1. Relative free energies in eV for intermediates in the reductive dechlorination of HCA in the gas phase (in aqueous solution). Anions labeled (vert) denote nascent species produced by vertical electron attachment; the italic values computed for such species are calculated as explained in the text. All values for species involving a free chloride ion include a correction of −0.23 eV.

We begin by considering the first reduction of HCA by a single electron. In the gas phase, the vertical EA is predicted to be −0.50 eV. The negative sign implies attachment is unfavorable (and thus the energy change in Figure 1 is positive). Burrow et al.[55] have estimated the EA for this process to be −0.05 eV based on a correlation between computed lowest unoccupied molecular orbital (LUMO) energies and negative vertical EAs in other chlorohydrocarbons. However, in the absence of an experimental measurement, it is difficult to decide which of the two numbers, if either, is likely to be more accurate—as this is a point of secondary interest, we do not attempt to further clarify the situation. When the geometry is allowed to relax in the gas phase, a stable radical anion, HCA$^{-\bullet}$, having C_{2h} symmetry with two long C−Cl bonds (2.384 Å) is found. The free energy of electron attachment in the gas phase is −1.27 eV. Gaines et al.[56] have reported an experimental value of −1.48 eV for this process, but the method employed did not include a mass analysis of detected ions, and Bartmess has questioned the

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reliability of this value.[57] Gas-phase dissociation of one chloride from relaxed $HCA^{-\bullet}$ to form infinitely separated $PCA^{\bullet}$ and Cl^{-} is endergonic, as expected since formation of small anions is highly disfavored in the gas phase. As already discussed above, the net gas-phase exergonicity for the overall process, reaction (E) of Table 2, is −0.96 eV at the CCSD(T) level, and −1.19 eV in Figure 1 where we include the best-estimate correction of −0.23 eV per chloride ion product.

Aqueous solution strongly stabilizes the anions, as expected, with chloride anion being particularly well solvated as a monatomic ion. In particular, dissociation of chloride in the final step is predicted to be exergonic with respect to relaxed $HCA^{-\bullet}$ by −1.19 eV in aqueous solution. The net exergonicity for reduction and fragmentation is −4.43 eV. Because of the computational expense, we have not followed the complete reaction coordinate for dissociation of chloride ion, but the higher energy of $HCA^{-\bullet}$ in aqueous solution compared to infinitely separated products $PCA^{\bullet}$ and Cl^{-} is consistent with the dissociation process proceeding without barrier, as is typically assumed. (Of course, if the dissociation is indeed barrierless, then the $HCA^{-\bullet}$ structure in Figure 1 is a nonstationary point along the reaction path on the liquid-phase potential of mean force.) In addition, if we start with the vertical species and stretch one of the long C−Cl bonds by 0.1 Å and shorten the other by the same amount, the energy in aqueous solution drops by 0.02 eV, which is further suggestive of no barrier to dissociation. [In an actual environmental process, the attached electron is not free and could well be transferred in an inner-sphere or heterogeneous process, which might be adiabatic (as compared to an outer-sphere process which is more likely to be vertical); from the point of view of HCA, an adiabatic process is less likely to lead to a species as highly excited as $HCA^{-\bullet}_{(vert)}$, but in the absence of a detailed characterization of the electron-transfer process (which will certainly vary from one reductant to the next) it is difficult to quantify this.]

The radical product $PCA^{\bullet}$ is stable to reaction with surrounding solvent because water is such a poor hydrogen atom donor. Indeed, using data in Table S-1 and the known heat of formation of a hydrogen atom (218.0 kJ mol^{-1} [37]) we can determine the 298 K C−H bond dissociation enthalpy in PCA to be 398.0 kJ mol^{-1}, which is so much smaller than the O−H bond dissociation enthalpy in water (498.8 kJ mol^{-1} [37]) that no H-atom transfer would be expected to occur. Of course, other better hydrogen-atom donors present in real environmental phases might react with $PCA^{\bullet}$, and such reactions may account for the very small amounts of PCA sometimes observed experimentally,[8] but we will not examine such reactivity and instead focus now on further reduction of $PCA^{\bullet}$.

Reaction schemes (a) and (b) of Chart 1 differ only in the time scale associated with loss of a chloride ion from PCA^{-}; reaction (a) involves direct dissociation while reaction (b) involves PCA^{-} as a stable intermediate. In the gas phase, the vertical EA is predicted to be 1.65 eV, and after relaxation of PCA^{-} to a structure resembling PCE with a chloride ion very loosely bound in an ion−dipole complex having a C−Cl distance of 3.300 Å, the net exergonicity is −3.04 eV.

Again, Gaines et al.[56] have reported a value for this process, namely −1.54 eV, but the criticism of Bartmess[57] noted above applies to this value as well. Given the extremely large difference between the measured and theoretical values (and the above documented good performance of the theoretical model for such estimates) the comments of Bartmess[57] seem reasonable. Complete dissociation of the ion dipole complex to produce chloride anion in the gas phase is predicted to be endergonic by 0.1 eV, making the overall exergonicity for the full process −3.17 eV.

In aqueous solution, the strong stabilization of free chloride anion again greatly increases the overall exergonicity of the dissociation. As in the initial reduction step discussed above, we find the solvated ion−dipole complex PCA^{-} to lie higher in energy than the separated products, and given the much looser nature of the ion−dipole complex in this case compared to HCA, it seems entirely likely that dissociation is rapid following vertical electron attachment to $PCA^{\bullet}$ (a solvated structure with the chloride ion 0.1 Å further from the PCE fragment than is found for the gas-phase ion−dipole complex PCA^{-} is predicted to be 0.09 eV lower in energy, supporting this hypothesis). The overall exergonicity for reduction and fragmentation is −6.40 eV relative to $PCA^{\bullet} + e^{-}$. The much larger exergonicity for this second reduction compared to the first is consistent with inferences that it is the first electron-transfer step or diffusion that is rate-determining for this process.

Focusing next on reaction scheme (c) of Chart 1, the gas-phase heterolytic dissociation of $PCA^{\bullet}$ into $PCE^{+\bullet}$ and a chloride anion is predicted to be endergonic by 5.99 eV. The free energy change associated with reduction of $PCE^{+\bullet}$ is −9.16 eV (this is the opposite of the ionization potential listed in Table 2 plus 0.02 eV difference in thermal contributions to the molecular free energies) to deliver the final products already discussed above.

In aqueous solution, the combined solvation free energies of $PCE^{+\bullet}$ and Cl^{-} are not large enough to render the heterolytic dissociation exergonic. Rather, it remains endergonic by 0.65 eV. Thus, this pathway is unlikely to contribute to any appreciable product formation.

We turn last to reaction scheme (d) of Chart 1. As already noted above, ejection of a chloride anion from the β-carbon of $PCA^{-}_{(vert)}$ (i.e., the carbon of the trichloromethyl group) forms a loose ion−dipole complex and is strongly exergonic. Ejection of a chloride anion from the α-carbon, on the other hand, forms singlet trichloromethylchlorocarbene (^{1}TCC), and is predicted to be endergonic (relative to $PCA^{-}_{(vert)}$) by 0.80 eV. In the gas phase, then, formation of ^{1}TCC would be unlikely.

In aqueous solution, however, formation of $^{1}TCC + Cl^{-}$ from $PCA^{-}_{(vert)}$ is predicted to be exergonic (relative to $PCA^{-}_{(vert)}$) by −0.38 eV. If α- and β-chloride elimination both proceed with very small or zero barriers, the relative rates for these two processes will be controlled by a complex assortment of factors, including solvent cage effects, intramolecular distributions of vibrational energies, etc. It is not a simple task to predict the branching ratio for the two paths. Moreover, it is not obvious that the electron-transfer step is vertical (depending on the nature of the interaction between $PCA^{\bullet}$ and whatever the actual reducing agent is, attachment of an electron may take place in a more adiabatic fashion). With all of these caveats in mind, it remains interesting to examine what the fate of ^{1}TCC might be if it is formed (see Figure 1).

As a carbene, ^{1}TCC can undergo intersystem crossing to its triplet state, ^{3}TCC. We compute the triplet to be higher in energy than the singlet by about 0.3 eV in both the gas phase and aqueous solution. Thus, even in the event of facile intersystem crossing, the equilibrium between the two will favor the singlet by about 5 orders of magnitude at room temperature.

One unimolecular rearrangement available to ^{1}TCC is a 1,2-chloride shift to generate PCE. We have located the transition state for this process, $^{1}TCC^{\ddagger}$, and find the free energy of

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(57) Bartmess, J. E. National Institute of Standards and Technology Webbook, URL: http://webbook.nist.gov.

activation to be just under 0.4 eV in either the gas phase or aqueous solution (this free energy of activation is about the same as is predicted at similar levels of theory for a 1,2-hydride shift in chloromethylchlorocarbene[58] but much lower than that found for the 1,2-fluoride shift in trifluoromethylfluorocarbene (1.1 eV),[59] indicating the greater nucleophilicity of the migrating chloride compared to fluoride). We can use transition-state theory [60] to estimate the unimolecular rate constant for this process,

$$k_{\mathrm{uni}} \approx k_{\mathrm{B}}T/h \exp(-\Delta G^{\ddagger}/RT) \qquad (3)$$

where k_B is Boltzmann's constant, T is temperature, h is Planck's constant, $\Delta G^{\ddagger}$ is the free energy of activation, and R is the gas constant. With a free energy of activation of 0.40 eV we obtain a rate constant for rearrangement of ^{1}TCC to PCE on the order of 10^6 s^{-1} at 298 K.

Such a rate constant is interesting insofar as it is not so high as to foreclose the possibility of ^{1}TCC reacting in a bimolecular sense. Carbenes react with many functional groups at diffusion-controlled rates.[61] If we assume an upper limit of 6×10^9 M^{-1} s^{-1} for the rate constant of a diffusion-controlled bimolecular reaction of a neutral species in water,[62,63] reactions of ^{1}TCC with species having millimolar or higher concentrations could have pseudo-first-order rate constants greater than 10^6 s^{-1} and thereby be competitive with or dominate unimolecular rearrangement. Of particular interest might be reactions with oxygen atom transfer agents that would lead to trichloroacetic acid (after hydrolysis of the initially formed acid chloride), a compound whose presence in drinking water is regulated by the United States Environmental Protection Agency. Small amounts of trichloroacetic acid have been detected in the reductive dechlorination of HCA under various conditions.[2,64]

As a consequence of the data in Figure 1, we conclude that reductive dechlorination of HCA takes place predominantly by stepwise transfer of 2 electrons, each of which is followed by barrierless chloride elimination, with the second elimination more exergonic than the first. Heterolytic dissociation of PCA$^{\bullet}$ can be ruled out as a reaction pathway on the basis of its high endergonicity. Fragmentation of PCA$^-_{\mathrm{(vert)}}$ to generate ^{1}TCC, on the other hand, may proceed to a small extent, and the interception of that reactive intermediate prior to its rearrangement to form PCE is possible.

Significance

Gas-phase free energies of reaction and aqueous one- and two-electron reduction potentials for reactions associated with the reductive dechlorination of hexachloroethane can be accurately calculated by electronic structure calculations with electron correlation included at the CCSD(T)/aug-cc-pVDZ//BPW91/aug-cc-pVDZ level and with aqueous solvation effects included by self-consistent reaction field theory at the SM5.42R/BPW91/DZVP level. When a small correction is made for a systematic error in the predicted electron affinity of the chlorine atom, predictions at this level are accurate to within 23 mV for four aqueous reduction potentials determined from experimental thermochemical data (or from best estimates of such data) and relevant to dechlorination of hexachloroethane. Simpler theoretical calculations that include electron correlation by density functional theory at the BPW91/aug-cc-pVDZ level are less successful owing to errors associated with this level's treatment of molecules characterized by highly delocalized charge or spin.

At the CCSD(T) + SM5.42R level, the mechanism of the reductive dechlorination of hexachloroethane in aqueous solution is predicted to proceed primarily via two successive single-electron transfers. After each transfer, one chlorine is eliminated (as a chloride ion) without a barrier. In the second step, which is the more exergonic, the elimination of a β-chloride ion proceeds to form perchloroethylene as the organic product. An alternative accessible pathway involves a less exergonic elimination of an α-chloride ion from pentachloroethyl anion to form trichloromethylchlorocarbene instead of perchloroethylene. The carbene is predicted to rearrange to perchloroethylene at a rate that is sufficiently slow that some rapid bimolecular reactions could be competitive.

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Appendix

Various standard state conventions are adopted in the literature for defining free energy changes in the gas phase and in aqueous solution. Since we consider processes taking place in both phases and since we need to convert theoretical standard-state free energies to thermodynamic standard-state free energies, this appendix details the relationships between conventions and defines our notation.

Two issues arise in working with free energies: the choice of zero of energy and the choice of standard state. In thermodynamics one avoids naming the zero of energy by working with balanced chemical equations, such as those which define free energies of formation (referring to the free energy required to assemble X at 1 bar and 298 K from its constituent elements in their *elemental* standard states). In quantum chemistry, it is convenient to establish a zero of energy and work with "absolute" free energies G(X). The *zero* of energy for the computation corresponds to all nuclei and electrons being infinitely separated and at rest.

The typical choice of standard state for a gas-phase system is an ideal gas at 1 bar pressure and 298 K.[65] We denote this choice of standard state as "$^{\mathrm{o}}$". Note that the free energy most typically tabulated for a given gas-phase molecule X is its standard-state free energy of formation, $G_{\mathrm{f}}^{\mathrm{o}}(\mathrm{X}_{(\mathrm{g})})$.

In aqueous solution, a common choice for the standard state for nonelectrolytes is a 1 molar (M) solution at 298 K and 1 bar pressure behaving as though at infinite dilution.[66] Thus, a standard-state free energy of a nonelectrolyte in solution (either $G^{\mathrm{o}}(\mathrm{X}_{(\mathrm{aq})})$ or $\Delta G_{\mathrm{f}}^{\mathrm{o}}(\mathrm{X}_{(\mathrm{aq})})$) may be computed as the sum of the standard-state gas-phase free energy and the free energy of transfer from the gas phase to solution under the appropriate standard-state conditions. Furthermore, a standard-state free energy of reaction in solution, $\Delta G^{\mathrm{o}}_{(\mathrm{aq})}$, for a reaction involving

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(58) Shustov, G. V.; Liu, M. T. H.; Rauk, A. *J. Phys. Chem. A* **1997**, *101*, 2509−2513.

(59) Cramer, C. J.; Hillmyer, M. A. *J. Org. Chem.* **1999**, *64*, 4850−4859.

(60) Kreevoy, M. M.; Truhlar, D. G. In *Investigation of Rates and Mechanisms of Reactions, Part I*, 4th ed.; Bernasconi, C. F., Ed.; Wiley: New York, 1986; pp 13−95.

(61) Moss, R. A.; Jones, M. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; John Wiley & Sons: New York, 1985; Vol. 3; pp 45−108.

(62) Hammes, G. G. *Principles of Chemical Kinetics*; Academic: New York, 1978; p 65.

(63) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; p 200.

(64) Weber, E. J. Personal communication.

(65) Denbigh, K. *The Principles of Chemical Equilibrium*, 4th ed.; Cambridge University Press: London, 1981; pp 256−257.

(66) Ben-Naim, A. *Solvation Thermodynamics*; Plenum: New York, 1987.

only nonelectrolytes can be computed as the gas-phase free energy of reaction plus the free energies of solvation of the products less the free energies of solvation of the reactants.

Electrolytes in aqueous solution, on the other hand, are typically treated by a different standard-state convention.[38,39] *In general*, the same conditions of concentration, temperature, and pressure are assumed, but the standard-state free energy of formation of an anion is defined as

$$\Delta G_f^{\phi}(A^-{}_{(aq)}) = \Delta G_f^{\phi}(A_{(aq)}) + \Delta G^{\phi}(A/A^-{}_{(aq)}) \quad (A.1)$$

where we denote the standard state for electrolytes as "$^{\phi}$", and $\Delta G^{\phi}(A/A^-{}_{(aq)})$ denotes the standard-state free energy change for the reaction

$$A_{(aq)} + {}^1/_2\, H_{2(g)} \rightarrow A^-{}_{(aq)} + H^+{}_{(aq)} \quad (A.2)$$

For a nonelectrolyte A, $\Delta G_f^{\phi}(A_{(aq)})$ is taken to be the same as $G_f^o(A_{(aq)})$ computed as described above. However ΔG_f^{ϕ} is taken as zero for both $H_{2(g)}$ *and* $H^+{}_{(aq)}$. By setting the standard state free energy of the aqueous proton equal to zero, this standard state convention differs from that for non-electrolytes (on a per proton or per electron basis) by the absolute potential, G^o_{NHE}, of the hydrogen electrode process producing one proton,

$${}^1/_2\, H_{2(g)} \rightarrow e^-{}_{(g)} + H^+{}_{(aq)} \quad (A.3)$$

which is 4.44 eV.[40] For electrochemical half reactions, this implies

$$\Delta G^o_{(aq)} = \Delta G^{\phi}_{(aq)} - (n - m)\Delta G^o_{NHE} \quad (A.4)$$

where n and m are the number of electrons appearing respectively on the left and right sides of the half reaction (typically, of course, one of m or n is zero).

If we combine the "$^{\phi}$" standard state for electrolytes with the "^{o}" standard state for gases and nonelectrolytes in some process under consideration, we label the result "$^{\phi'}$". We can also consider using the "^{o}" standard state even for electrolytes. While this is convenient computationally, reduction potentials in standard tabulations are derived from the Nernst equation using the differing conventions for electrolytes and nonelectrolytes (the "$^{\phi}$" standard state). Furthermore, *in the particular case of compiled values of one- and two-electron reduction potentials for chlorinated hydrocarbons*, standard state chloride and proton concentrations of 10^{-3} and 10^{-7} M, respectively, tend to be employed (the proton concentration implies pH = 7). Free energies of reaction for a different choice of standard-state concentration(s) are related to the more conventional 1 M standard state according to

$$\Delta G^{\phi'}_{(aq)} = \Delta G^{\phi}_{(aq)} + RT \ln(Q^{\phi'}/Q^{\phi}) \quad (A.5)$$

where R is the gas constant, T is the temperature, and Q is the reaction quotient (i.e., the ratio of concentrations that appear in the equilibrium constant) evaluated with all species at their standard-state concentrations.

Note that the e^- in all half reactions is always considered to be a gas-phase electron in the G^o or G_f^o scales (it has a value of zero for both), whereas all the electrons are canceled out in using the ΔG^{ϕ} or $\Delta G^{\phi'}$ scales.

As a final point, note that the SM5.42R solvation model computes free energies of hydration $\Delta G^*_{hyd}(X)$ using a 1 M standard-state concentration for X in *both* the gas phase and solution. This differs from the gas-phase concentration of 1/24.8 M for an ideal gas in the more conventional one bar standard state. To derive free energies of reaction in aqueous solution consistent with all of the relevant standard states listed above, computational free energies in solution are calculated as

$$G^o(X_{(aq)}) = G^o(X_{(g)}) + \Delta G^*_{hyd}(X) + RT \ln(24.8) \quad (A.6)$$

Equation A.6 is entirely analogous to eq A.5 in accounting for a change in standard-state concentration. Note that $\Delta G^*_{hyd}(X)$ is the quantity called G^o_S in reference 20, where only the 1 M standard state is used, but we avoid calling it that here because we use the 1 bar standard state for gases in this paper.

Supporting Information Available: Tables of computed and experimental thermochemical quantities. (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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