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Reductive Dechlorination of Trichloroethylene: A Computational Study

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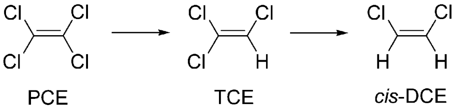
Vitamin B_{12} catalyzes the reductive dechlorination of several ubiquitous pollutants including the conversion of trichloroethylene (TCE) to ∼95% *cis*-1,2-dichloroethylene (DCE) and small amounts of *trans*-DCE and 1,1-DCE. The origins of this unexpected selectivity were investigated using density functional and coupled-cluster theory. At all levels of theory considered, the initially formed trichloroethylene radical anion is an unstable species. Breakage of one of the three C−Cl bonds during the dissociative process gives the most stable ion complex when the two remaining chlorines occupy a cis geometry. Once formed, the *cis*-1,2-dichloroethen-1-yl radical is about 6 kJ/mol more stable than the corresponding trans radical and 21 kJ/mol more stable than the 1,1-dichloroethen-2-yl radical. The calculated relative energies can be rationalized by delocalization of the unpaired electron over the nonbonding orbitals of the α-chlorine. The computed geometries of the radicals suggest significant interactions between the orbital occupied by the unpaired electron and the σ^* orbital of the β C−Cl bond trans to the radical. The barrier for interconversion of the two 1,2-dichlorinated vinyl radicals lies between ∼30−40 kJ/mol depending on the level of theory. The reactivities of the three radicals with respect to hydrogen atom abstraction from methanol (C−H or O−H) as well as chlorine elimination were investigated. All three radicals show a strong preference for abstraction of the α-hydrogen atom of methanol (17−25 kJ/mol), with a significant positive reaction energy for chlorine elimination (60−80 kJ/mol). These results are discussed further in relation to the experimentally observed product distribution.

Introduction

Chlorinated organic compounds are priority pollutants that are prevalent worldwide. Among these contaminants of soil and groundwater are perchloroethylene (PCE, PERC, tetrachloroethene) and trichloroethylene (TCE),[1] two compounds that have been commonly used as solvents in various industrial settings.[2] PCE and TCE have long environmental half-lives due, in part, to their very slow oxidative breakdown under aerobic conditions.[3] Furthermore, these compounds cause tumors in animals and are suspected human carcinogens.[4] In the past decade, two reductive dechlorination processes that rely on vitamin B_{12} for catalysis have been discovered. In 1991, Wackett and Gantzer reported that B_{12} in the presence of a strong reductant such as Ti(III) citrate can reductively dechlorinate PCE to TCE, followed by subsequent transformation of TCE to predominantly *cis*-1,2-dichloroethylene (*cis*-DCE) and small amounts of *trans*-DCE and 1,1-DCE, as shown in eq 1.[5] More recently, Diekert and co-workers purified a reductive B_{12}-dependent dehalogenase from *Dehalospirillum multivorans*, an anaerobic microorganism that couples reduction of PCE and TCE to energy metabolism.[6] The enzyme dechlorinates TCE to produce *cis*-dichloroethylene, giving similar stereo- and regioselectivities to those shown in eq 1.



(1)

Several reports have suggested that the nonenzymatic process involves electron transfer from the Co(I) form of vitamin B_{12} to PCE.[7−9] In the gas phase, low-energy electron scattering studies have provided vertical electron attachment energies for PCE.[10] These measurements indicate that the electron initially occupies the π^* orbital, followed by transfer to a σ^* orbital of the C−Cl bonds leading to chloride anion elimination.[11] The trichlorovinyl radical so produced may be converted to TCE by either hydrogen atom abstraction from a suitable source or reduction to the anion followed by protonation. In the reductive dechlorination of TCE, three isomeric dichloroethenyl radicals **4**−**6** would be formed (Scheme 1). The fate of these radicals will largely depend on the reaction conditions. In the presence of sufficiently reactive hydrogen atom donors, hydrogen atom transfer will lead to the corresponding dichloroethylenes **7**−**9**. Alternatively, these same products could also be obtained through single-electron reduction of radicals **4**−**6** and subsequent protonation of the resulting anions.

Reductions of **1** and other trichlorinated alkenes by B_{12} show surprisingly selective formation of *cis*-1,2-dichlorinated products (e.g., **7** from **1**), with only small amounts of the trans compounds (e.g., **8**) and 1,1-dichlorinated ethylenes (e.g., **9**).[5,7,8,12] This product distribution is determined by the relative rates of the various steps in Scheme 1. The regioselectivity of chloride elimination leading to either 1,2- or 1,1-disubstituted products will be controlled by the relative rates for conversion to vinyl radicals **4**−**6**. The stereoselectivity for the formation of **7** and **8**, however, may be controlled at two different stages. If the stereoisomeric vinyl radicals **4** and **5** are in rapid equilibrium relative to the rate of hydrogen atom abstraction (or reduction), then the product ratio of **7** to **8** will be under Curtin−Hammett control. In this scenario, only the difference in the transition-state energies for the conversions of **4** to **7** and **5** to **8** will determine the product distribution. In contrast, if the barriers

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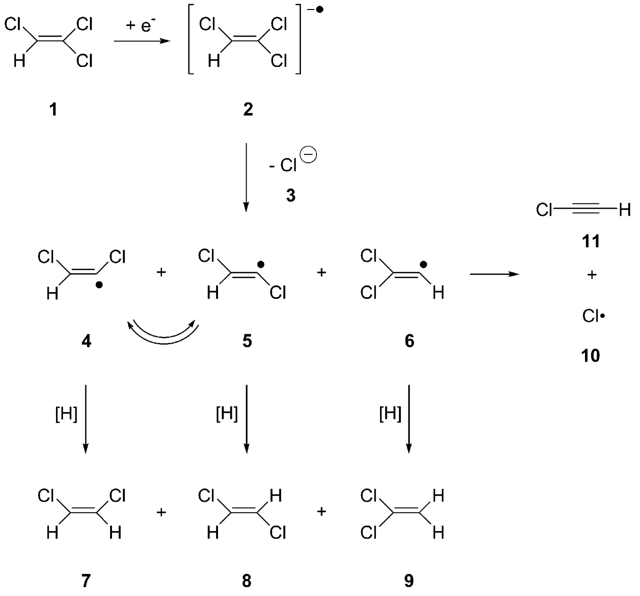
SCHEME 1



of hydrogen atom abstraction (or one-electron reduction) are low compared with the interconversion barrier, then the product distribution will be governed by the relative concentrations of **4** and **5** and thus by the mechanism of their formation from **1**. To understand the factors leading to the observed product distribution, we report here density functional theory and ab initio studies that address (a) the fate of radical anion **2** formed after electron transfer to **1** and the relative stabilities of the complexes of the dichloroethenyl radicals and eliminated chloride anion; (b) the relative stability of radicals **4**−**6**; (c) the thermochemical effort required to form chloroacetylene **11** and chlorine **10**; and (d) the trapping of radicals **4**−**6** with methanol as a model hydrogen atom donor. The results of these studies provide explanations for previous experimental observations and enhance our understanding of the factors governing product distribution.

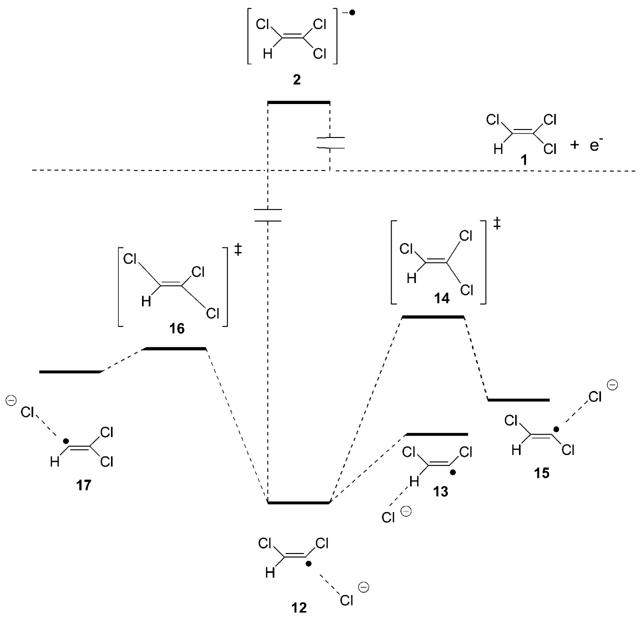


Figure 1. Potential energy surface for the dissociative one-electron reduction of trichloroethylene (**1**).

Computational Methods

The potential energy surface of radical anion **2** has been explored using the split valence 6-31+G(d,p) basis set in combination with the hybrid density functional Becke3LYP.[13−15] Relative energies have then been calculated using the Becke3LYP functional in combination with the aug-cc-pVTZ basis set.[16] Additional consideration of differences in unscaled B3LYP/6-31+G(d,p) zero-point vibrational energies gives the energies referred to as “B3LYP/aug-cc-pVTZ” throughout this article. Relative energies have also been calculated at the UCCSD(T)/cc-pVTZ level of theory for some of the structures. Combination with differences in unscaled B3LYP/6-31G(d,p) zero-point vibrational energies gives the results referred to as “CCSD(T)/cc-pVTZ”. For the larger system, the UCCSD(T) calculations were performed using the smaller cc-pVDZ basis set. The effects of the surrounding solvent were included through single-point calculations at the Becke3LYP/6-31+G(d,p) level of theory using the CPCM continuum solvation model.[17] The UAHF model has been used for the definition of the solute cavity.[17b] To mimic the situation in mixtures of water ($\epsilon = 78.4$) and 2-propanol ($\epsilon = 18.3$) typically used in radical trapping experiments,[7,8] the dielectric constant was set to $\epsilon = 32.63$ (methanol). The combination of the CPCM solvation free energies with the gas-phase B3LYP/aug-cc-pVTZ values gives the results referred to as “ΔG_{sol}”. DFT and coupled-cluster theory methods have been recently validated in reductive dechlorinations of other halogenated pollutants by comparison of calculated and experimental data where available.[18] All neutral open-shell systems were treated in the same manner as described above for radical anion **2** with the exception that the 6-31G(d) basis set was used for geometry optimization, frequency calculations, and CPCM calculations. The charge distribution has been characterized through a natural population analysis.[19] All calculations have been performed with Gaussian 98.[20]

Results and Discussion

One-Electron Reduction of Trichloroethylene (1). At all levels of theory considered in this study, the trichloroethylene radical anion **2** is an unstable species, consistent with the experimentally measured[10] negative vertical electron affinity of −0.59 eV for this species. It is interesting that the most favorable state of radical anion **2** at the B3LYP/aug-cc-pVTZ level of theory is of A′ symmetry. This is in contrast to earlier expectation[11] as well as the fact that the lowest-lying vacant orbital in trichloroethylene **1** (mo33) is of A″ symmetry (π^*). The corresponding A″ state of radical anion **2** is predicted to be less stable than the A′ state at the B3LYP/aug-cc-pVTZ level of theory. However, at the CCSD(T)/cc-pVTZ level, the reverse order of stability is found. It is important to note that both the vertical electron affinity as well as the relative energies of the two anion states depend substantially on the choice of basis set and theoretical method (see Table 5 in Supporting Information for details).[21] Geometry optimization of **2** obtained through vertical electron transfer to trichloroethylene **1** leads directly to complex **12**, which also is the most stable species on this part of the potential energy surface (Figure 1). The preferred formation of complex **12** over alternatives such as **15** or **17** may be a reflection of the NLUMO (next lowest unoccupied molecular orbital) structure of trichloroethylene **1** (orbital 34), which consists in large part of the σ^*(C−Cl) bond that is broken during geometry optimization. The character of complex **12** is not fully reflected in the Lewis structure shown in Figure 1 in that the formal chloride anion carries some of the unpaired spin

TABLE 1: Potential Energy Surface (kJ/mol) for Dissociative One-Electron Reduction of Trichloroethylene (1)

structure	B3LYP/aug-cc-pVTZ	CCSD(T)/cc-pVTZ	ΔG_{sol}
1 + e^-	+94.1	+14.3	
2 (A′)	+129.7	+215.4	+165.5
2 (A″)	+156.6	+153.6	+188.5
12	0.0	0.0	0.0
13	+14.6	+8.3	+5.7
14	+39.7	+32.2	+72.0
15	+19.7	+16.3	+26.9
16	+23.8	+28.4	+52.4
17	+23.4	+25.5	+43.2
3 + **4**	+79.4	+85.1	−0.3

density (0.3) and not a full negative charge (−0.63*e*). It might therefore be more appropriate to consider **12** to be a species with an extended three-electron C−Cl bond. Full cleavage of this bond to give **13** is less favorable by 14.6 kJ/mol at the B3LYP/aug-cc-pVTZ level. Complex **15** including a *trans*-dichloroethenyl radical substructure is less favorable than **12** by 19.7 kJ/mol and can be reached through transition state **14**. The chloride exchange process through **14** can be described as a concerted nucleophilic vinylic substitution at the formal radical center in **12**. The barrier for this process amounts to almost 40 kJ/mol at the B3LYP/aug-cc-pVTZ level. A much lower barrier of +23.8 kJ/mol is found for the isomerization of **12** to complex **17**. In this case, the transition state **16** and product complex **17** are almost isoenergetic. Dissociation of complex **12** to chloride **3** and vinyl radical **4** is strongly endothermic in the gas phase but practically thermoneutral in solution. These calculations were conducted in the gas phase and by applying a continuum solvation model, but radical anions have also been observed experimentally in solution during reductive dechlorinations of organohalides.[22] Furthermore, recent experimental studies have indicated that complexes between radicals and anions are not confined to the gas phase but may also be formed in dissociative one-electron-transfer reactions in polar solvents.[23]

Isomerization of **12** to less-favorable complexes **15** and **17** is possible in the gas phase through nucleophilic attack of the formal chloride anion at the radical center. With respect to earlier studies on nucleophilic substitution reactions involving chloride, a large solvent effect is expected for this type of reaction in protic solvents.[24−26] According to the differential solvation free energies of complex **12** and transition states **14** and **16** obtained with the CPCM model, both substitution pathways will face substantially larger barriers in a protic solvent such as methanol than in the gas phase. Considering a calculated solution barrier of more than 70 kJ/mol for the interconversion of **12** and **15**, we find it unlikely that the substitution processes shown in Figure 1 play any practical role in the chemistry of radical−anion complex **12** in protic solvents.

Relative energies and barrier heights computed at the CCSD(T)/cc-pVTZ level are very similar to those obtained at the B3LYP/aug-cc-pVTZ level, with one exception. Whereas the adiabatic electron affinity of **1** is predicted to be substantial at the B3LYP/aug-cc-pVTZ level (+94.1 kJ/mol), a much smaller value is obtained at the CCSD(T)/cc-pVTZ level (+14.3 kJ/mol) (see Table 5 in Supporting Information for additional details). A similar observation has been made by Patterson et al. in their recent study of the one-electron reduction of hexachloroethane (HCA).[18]

The calculated relative stabilities of radical−anion complexes **12**, **15**, and **17** in Table 1 agree with a recent study reporting one-electron redox potentials for dissociative electron transfer to TCE calculated from thermodynamic data. This latter study arrived at a less negative potential for the conversion of TCE to the *cis*-dichloroethen-1-yl radical and chloride anion (−0.67 V) compared to that for the formation of the *trans*- or 1,1-dichlorinated radical (−0.69 and −1.0 V, respectively).[27,28] The redox potential for reduction of TCE to the *cis*-dichloroethenyl radical reported in this study (−0.67 V)[27] is close to that of the Co(I)/(II) potential of B_{12} (−0.61 V),[29] in line with electron transfer from the reduced form of B_{12}. Such a process is likely to involve an innersphere electron-transfer pathway, as observed for the reaction of reduced cobalt porphyrins as well as cob(I)alamin with certain alkyl halides.[30] An inner sphere electron-transfer pathway is also suggested by remediation studies reporting that other strong reductants such as Ti(III) citrate (ca. −0.63 V at pH 8)[31] do not appreciably react with TCE until the addition of vitamin B_{12}.[7] In these remediation strategies, Ti(III) citrate serves to reduce vitamin B_{12} to its Co(I) state, which then initiates dechlorination by electron transfer to TCE.

TABLE 2: Relative Energies (kJ/mol) for Dichloroethenyl Radicals 4−6, the Transition State TS(4/5) for Interconversion between 4 and 5, Chloroacetylene (11) + Chlorine Atom (10), and Dichloroethylenes 7−9

theoretical method	4	5	6	TS(4/5)	10+11	7	8	9
B3LYP/aug-cc-pVZT	0.0	+6.7	+24.0	+30.6	+103.8	0.0	+0.1	+5.2
CCSD(T)/cc-pVDZ	0.0	+5.3	+21.1	+43.5	+88.5	0.0	−0.9	+3.1
CCSD(T)/cc-pVTZ	0.0	+6.5	+20.7	+39.1	+92.6	0.0	+0.3	+3.2
ΔG_{sol}	0.0	+4.5	+26.1	+28.4	+106.1	0.0	+2.1	+15.6
experimental								
$\Delta\Delta H_f$[35]						0.0	+2.6	+5.4

Relative Stability of Dichloroethenyl Radicals 4−6. The relative energies of radicals **4**−**6** are given in Table 2. At all levels of theory considered here, *cis*-1,2-dichloroethen-1-yl radical (**4**) represents the energetically most favorable isomer. The energy difference between **4** and the corresponding trans isomer **5** is relatively independent of the level of theory used and amounts to around 6.5 kJ/mol. Moreover, thermochemical corrections to relative energies are fairly small, and relative enthalpies at 298 K are almost identical to relative energies computed at 0 K. The preferential stability is surprising at first sight because *cis*-1,2-disubstituted alkenes are often less stable than the corresponding trans isomers because of electrostatic and steric factors. The different stabilities in this study can be attributed to stereoelectronic effects involving the radical center, the chlorine lone pairs, and the σ^*(C−Cl) orbitals (see below). The 1,1-dichloroethen-2-yl radical (**6**) is significantly less stable than **4** or **5** and is located approximately 21 kJ/mol above **4**. This situation is practically unaffected by protic solvents. It is interesting that the energy difference between **4** and **5** is significantly smaller than the difference between **12** and **15**. This suggests that the presence of a nearby chloride anion in the latter species significantly alters the relative energies of the regioisomeric radicals.[32]

The barrier for interconversion between **4** and **5** shows a significant dependence on the level of theory. Whereas the best estimate obtained at the Becke3LYP level sets the inversion barrier at around +30 kJ/mol, significantly higher values are obtained at the CCSD(T) level. Considering the difference between CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ barriers, this might, in part, be due to an insufficiently large basis set for the CCSD(T) calculations (see Table 2 in Supporting Information for differences in $\langle S^2\rangle$ values for the Becke3LYP and CCSD(T) calculations). Even the Becke3LYP barrier is, however, considerably higher than that found for the parent vinyl radical of ∼12 kJ/mol.[33a−c] Earlier experimental studies have reported that the inversion barrier of vinyl radicals depends strongly on the α-substituent.[33d] Particularly high barriers were

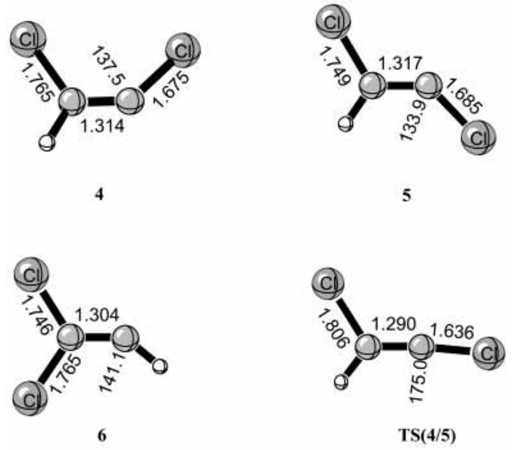
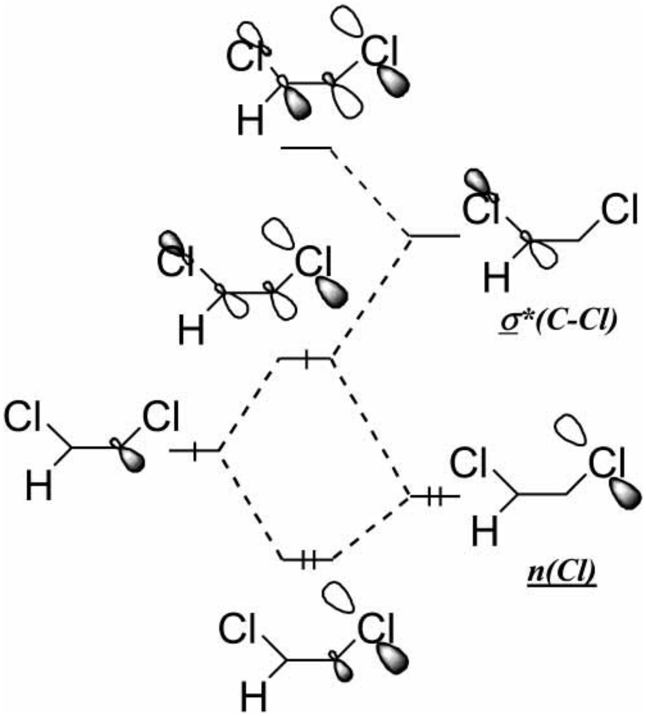


Figure 2. Structures of radicals **4**−**6** and transition state **TS(4/5)** as calculated at the Becke3LYP/6-31G(d) level of theory. All distances are given in Å, and all angles, in degrees.

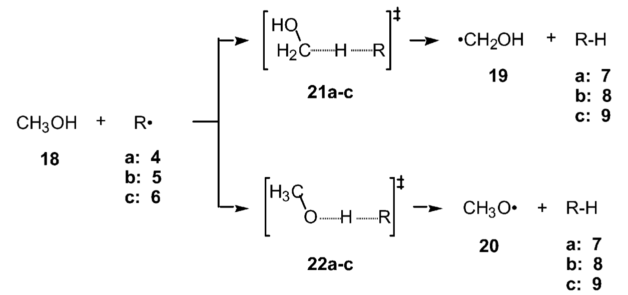
SCHEME 2



found for halogen-substituted systems whereas low barriers oreven linear vinyl radicals were reported for substituents containing large π-systems. Hence, the relatively high inversion barriers found here are consistent with these experimental studies.

The structures for radicals **4**−**6** as well as for transition state **TS(4/5)** are shown in Figure 2. The most notable feature of the structures of **4** and **5** is the variable length of the C−Cl bonds. Whereas the bond length of the α(C−Cl) bond is 1.675 Å in **4**, the C−Cl bond adjacent to the radical center is significantly longer at 1.765 Å. This difference is largest in **TS(4/5)** and smallest in trans isomer **5**. The short α(C−Cl) bond points to a stabilizing interaction between the SOMO located at the radical center and one of the chlorine lone-pair orbitals (Scheme 2). As a consequence, the α-Cl atoms carry up to 12% of the unpaired spin density in radicals **4** and **5**. This type of stabilizing interaction is possible only in **4** and **5** but not in **6** and appears to be the main reason for the higher energy of the latter isomer. The variations observed for the β(C−Cl) bond length are indicative of an additional orbital interaction involving the $\beta-\sigma^*$(C−Cl) orbital and the radical center. This interaction appears to be stronger in **4** than in **5** on the basis of the longer β(C−Cl) bond in **4**.

SCHEME 3



Chloroacetylene has been detected during reductive dechlorination of TCE,[12,34] and it has been proposed[7] that this product may be formed by dissociation of chloroethenyl radicals to chloroacetylene (**11**) and chlorine radical **10**. The reaction energies calculated for this process are, however, positive at all levels of theory investigated here, as might be expected given the reactivity of radicals toward acetylenes. The best estimate for the reaction energy obtained at the CCSD(T)/cc-pVTZ level of theory is +92.6 kJ/mol, whereas the B3LYP/aug-cc-pVTZ value is somewhat higher at +103.8 kJ/mol. Again, solvent effects have no major influence on this result. Considering that the transition-state energies are, if anything, even higher than the thermodynamic reaction energies, chlorine elimination from radicals **4**−**6** appears unlikely.

Product Stabilities. The relative energies for the product dichloroethylenes **7**−**9** are given in the last three columns of Table 2. At most computational levels, *cis*-1,2-dichloroethylene (**7**) is predicted to be the most stable isomer. The corresponding trans isomer **8** is, however, almost as stable as **7**. The least stable compound is 1,1-dichloroethylene (**9**), which is located only +3.2 kJ/mol above **7**. Thermochemical corrections to relative energies are again quite small, and relative enthalpies at 298 K are almost identical to relative energies at 0 K. Solvent effects have little influence on the relative stabilities of **7** and **8** but decrease the stability of **9** quite significantly. A recent exhaustive evaluation of the reported experimental stabilities of the three dichlorinated ethylenes recommends the relative stabilities shown in Table 2.[35] The computed relative stabilities are in excellent agreement with the experimental values and differ by no more than ± 3 kJ/mol (0.7 kcal/mol); we thus estimate the residual errors of the computed relative energies to be ± 3 kJ/mol.

Reaction Barriers for Hydrogen Abstraction from Methanol. In principle, hydrogen atom transfer reactions between radicals **4**−**6** and methanol (**18**) can proceed either through attack at the O−H or the C−H bond (Scheme 3). Attack at the C−H bond is usually preferred because of the higher homolytic bond-dissociation energy of the O−H bond. Using the experimental heats of formation of the methanol-1-yl radical (**19)** and the methoxy radical (**20**), this difference in thermodynamic stability amounts to +26 ± 8 kJ/mol in favor of **19**.[36,37] The calculated value at the B3LYP/aug-cc-pVTZ level of theory is +27.2 kJ/mol. Including thermal corrections to 298 K yields a value of $\Delta\Delta H_f(298) = +26.5$ kJ/mol, in good agreement with the experimental value. A somewhat smaller value of $\Delta\Delta H_f(298) = +21.9$ kJ/mol is obtained using the CCSD(T)/cc-pVDZ relative energies. Attack of the *cis*-1,2-dichloroethen-1-yl radical (**4**) at the methanol C−H bond leads through transition state

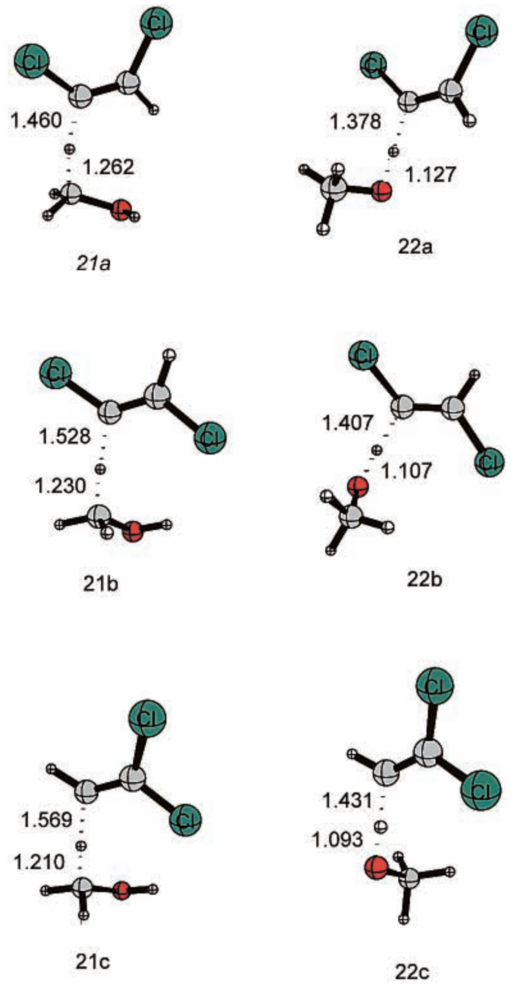


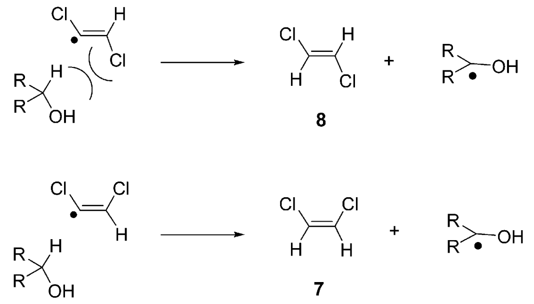
Figure 3. Structures of transition states for C−H abstraction (**21a**−**c**) and for O−H abstraction (**22a**−**c**) calculated at the Becke3LYP/6-31G(d) level of theory. All distances are given in Å, and all angles, in degrees.

TABLE 3: Activation and Reaction Energies (kJ/mol) for Hydrogen Transfer Reactions between Dichloroethenyl Radicals 4−6 and Methanol (18)

structures	B3LYP/aug-cc-pVTZ	CCSD(T)/cc-pVDZ	ΔG_{sol}
4 + **18**	0.0	0.0	0.0
21a	+15.3	+13.5	+17.4
7 + **19**	−54.1	−58.0	−63.4
22a	+13.8	+15.5	+33.5
7 + **20**	−26.9	−35.4	−24.2
5 + **18**	0.0	0.0	0.0
21b	+11.3	+11.7	+28.1
8 + **19**	−60.7	−64.1	−65.7
22b	+14.3	+13.6	+35.7
8 + **20**	−33.5	−41.6	−26.5
6 + **18**	0.0	0.0	0.0
21c	+8.7	+11.4	+23.8
9 + **19**	−72.9	−76.0	−73.9
22c	+10.2	+10.2	+30.8
9 + **20**	−45.7	−53.5	−34.7

21a to the methanol radical (**19**) whereas attack at the O−H bond through transition state **22a** yields the methoxy radical (**20**) (Figure 3). The gas-phase reaction barriers calculated for these processes are surprisingly similar, with a slight preference for O−H abstraction at the B3LYP/aug-cc-pVTZ level and a small preference for C−H abstraction at the CCSD(T)/cc-pVDZ level (Table 3). In any case, the differences are far less than what would be expected on the basis of the strongly different reaction energetics. Inclusion of solvent effects, however, leads to an increase in the reaction barrier for O−H abstraction of around 20 kJ/mol. This implies that the experimentally observed preference for C−H abstraction in polar media is mainly due to the unfavorable solvation of transition states for O−H abstraction. This difference in solvation free energy may be due to the energy required to break the hydrogen bond in which the reacting proton of the hydroxy group is engaged in protic media.[38]

SCHEME 4

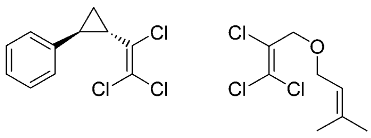


The activation and reaction energies calculated for radical **5** are mostly similar to those obtained for **4**, but the solvent effect on the barrier for C−H abstraction is significantly larger. This might be a consequence of the intramolecular hydrogen bond formed in transition state **21b** between the methanol hydroxy group and one of the chlorine atoms of **5** (Figure 3). As a result, the differences between O−H and C−H abstraction barriers in solution are not as large as those for radical **4**. A similar conclusion can be reached for abstraction reactions of radical **6** in the gas phase and in solution.

Implications for the Mechanism of B_{12}-Catalyzed Dechlorination of Trichloroethylene. The computational studies reported in this article provide explanations for several experimental observations and allow us to distinguish between a number of possible mechanistic scenarios that have been put forth for the B_{12}-catalyzed reductive dechlorination of TCE. Several reports have proposed that one-electron transfer from the strongly reducing Co(I) form of vitamin B_{12} (cob(I)alamin) to the electrophilic alkenes PCE and TCE initiates the reductive dechlorination of these compounds.[7,8,12] Concerted or stepwise chloride elimination would then produce a series of isomeric chloroethenyl radicals, as shown in Scheme 1. Currently, our theoretical results do not yet address whether one-electron transfer from cob(I)alamin to TCE is energetically feasible.[39] If such a reaction would occur, as suggested by spectroscopic studies with TCE and other trichlorinated alkenes,[7,8] a dissociative electron-transfer reaction would result, as shown by the calculated instability of radical anion **2**. Furthermore, the computations indicate that the lowest-energy ion complex obtained upon vertical electron transfer and chloride elimination has a >25 kJ/mol propensity for cis disposition of the two chlorines. This preference is also found in the relative energies of the stable chlorinated ethenyl radicals that are formed as products of the dissociative electron transfer, although the difference between cis and trans radicals **4** and **5** is much smaller, ~4−6 kJ/mol (Table 2).

A number of explanations have been suggested for the strong selectivity for *cis*-DCE in the reductive dechlorination of TCE. Building on previous work by Kampmeier and co-workers,[40] one hypothesis involved a higher reactivity of the *cis*-DCE radical (**4**) relative to **5** on the basis of steric interactions between the chlorine at C2 and the approaching hydrogen atom donor (Scheme 4).[7] This kinetic argument implied rapid interconversion of **4** and **5** to account for the ~20:1 selectivity for **7**. The

CHART 1



23 **24**

theoretical transition-state energies calculated in the gas phase, however, do not provide a lower barrier for hydrogen atom abstraction by **4** than by **5** from a model alcohol (methanol). Only when CPCM solvation energies were combined with the gas-phase results did a significant difference in the transition-state energies for the reactions of **4** and **5** with methanol appear. This suggests that the cis selectivity is not due to steric interactions but rather to differential solvation. Moreover, the reductive B_{12}-catalyzed dechlorination of other trichlorinated alkenes such as **23** and **24** (Chart 1**)** also showed strong cis selectivity[8] even though the cis-substituted radical should now be less reactive than if steric factors were to control selectivity.

The barrier for interconversion of **4** to **5** (≥28 kJ/mol, Table 1) is higher than the barrier for hydrogen atom abstraction by **4** from methanol (13−17 kJ/mol) at all levels of theory (Figure 4). According to these data, the rate constant for hydrogen atom abstraction will be larger than that for isomerization. However, because the latter reaction is a unimolecular process ($\sim 10^7$ s^{-1} for $\Delta G^{\ddagger} = 30$ kJ/mol at 298 K) whereas hydrogen atom abstraction is bimolecular, the actual relative rates of these two competing transformations of **4** will be dependent on the concentration of the alcohol. A different picture is seen for **5**. Depending on the level of theory, the barrier for isomerization to **4** varies between ∼24−38 kJ/mol. If the value for the solvated model is taken (24 kJ/mol), then the barrier for isomerization is now lower than that for hydrogen atom abstraction from methanol (∼28 kJ/mol, Figure 4). Therefore, the significantly higher barrier for hydrogen atom abstraction by **5** and the possibility that **5** may interconvert to **4** are two more factors that would favor the formation of **7** over **8**.

The computations reproduce the experimentally determined cis selectivity and provide explanations for this previously puzzling observation. In addition, the calculated energy differences for the various intermediates and transition states may be compared with the experimentally observed ratio of **7** to **8**. Consideration of two extreme energy profiles can help clarify the factors controlling the relative amounts of these two products. If the isomeric radicals **4** and **5** rapidly interconvert relative to the rate of hydrogen transfer by methanol, then the product ratio should be governed entirely by the difference in the activation energies for product formation. This difference, taken from the ΔG_{sol} data in Table 3, corresponds to about 10 ± 3 kJ/mol, which would predict a ratio of between 17:1 and ∼180:1 for **7**:**8**. Thus, for this scenario, the experimentally observed ratio of ∼20:1 falls within the error limit of the calculated ratios. On the other extreme, hydrogen atom abstraction by both **4** and **5** could be much faster than isomerization (e.g., at high methanol concentrations), in which case the ratio of **7** to **8** would be dependent only on the relative quantities of **4** and **5** produced. It is difficult to determine the relative amounts of these radicals formed during the initial dissociative electron transfer because relative rates for their generation are not available and are not readily calculated. It is interesting, however, to compare the energy differences between the geometry-optimized complexes produced by dissociative electron transfer. Thus, the energy difference between **12** and **15**, producing **4** and **5**, respectively, is ∼27 ± 3 kJ/mol (ΔG_{sol}, Table 1), corresponding to a ratio of $\sim 2 \times 10^4$:1 (for 27 kJ/mol) for **4**:**5**. If the two radicals do not interconvert, this would favor **7** by an unrealistically large margin. Thus, purely on the basis of a mechanism shown in Scheme 1 and the relative energies for the species in Figure 1, interconversion of **4** and **5** would be necessary after their formation from **12** and **15**, respectively, to account for the observed product ratios. A potential caveat should be pointed out, however. As discussed in more detail below, the transformations in Scheme 1 may not be the only pathways to products **7** and **8**, and alternative pathways could complicate a quantitative comparison of the experimental product ratio with the energies listed in Tables 1−3.

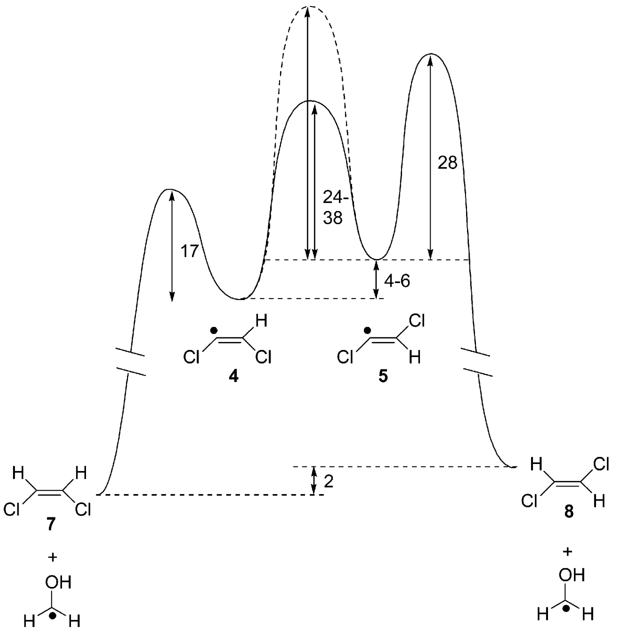
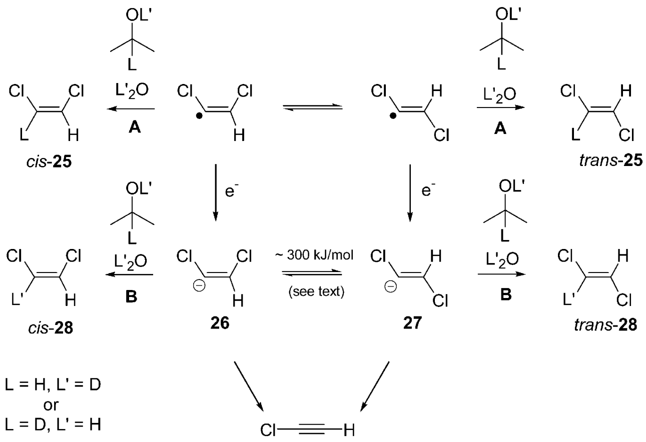


Figure 4. Graphical presentation of the calculated barriers for the different processes available to radicals **4** and **5**. The dashed and solid barriers between **4** and **5** correspond to the values calculated at the CCSD(T)/cc-pVDZ and ΔG_{sol} levels of theory, respectively (Table 2). All energy differences are given in kJ/mol.

Mechanism of Chloroacetylene Formation. An apparent difference between the computational and the experimental studies involves chloroacetylene. Chloroacetylene has been detected in the B_{12}-catalyzed dechlorination of TCE.[12,34] Its formation has been proposed to occur by chlorine elimination from the 1,1-dichloroethen-2-yl radical (**6**),[7] but the current work suggests that the conversion of radicals **4** or **5** into chloroacetylene and a chlorine atom would be uphill, with a minimum barrier of around 90−100 kJ/mol. Even for radical **6**, which is significantly higher in energy than **4** and **5** and might be expected to be more reactive toward elimination, the reaction energy for chlorine elimination is significantly higher than the barrier for hydrogen atom abstraction (Tables 2 and 3). Thus, in comparison with the other pathways available to these radicals, chloroacetylene formation is by far the least-favorable pathway.[41]

The apparent discrepancies between experiment and theory in the formation of chloroacetylene may be attributed to a second competing reaction manifold. The product dichloroethylenes can be produced from chlorinated ethenyl radicals **4**−**6** by hydrogen atom abstraction *or* by reduction to their anions (**26** and **27**, Scheme 5) followed by protonation. This latter pathway is supported by deuterium-labeling studies using *i*-PrOD/D_2O or 2-d_1-*i*-PrOH/H_2O solvent mixtures, which suggest that two pathways for product formation must be operating.[7,8] In one

SCHEME 5



pathway, DCE products **25** are derived from chloroethenyl radicals that abstract hydrogen or deuterium atoms from the C2 carbon of *i*-PrOD and 2-d_1-*i*-PrOH, respectively (Scheme 5, pathways A). The calculated activation energies for hydrogen atom abstraction from C−H versus O−H bonds discussed above support this interpretation of the labeling studies. However, products **28** are also observed and must be formed by a pathway that leads to the transfer of a deuteron from *i*-PrOD/D_2O or a proton from 2-d_1-*i*-PrOH/H_2O (pathways B). In other words, a significant fraction of the products must be derived from anionic intermediates.[42] These vinyl anions could therefore be the source of chloroacetylene observed experimentally by the elimination of chloride.[43] Alternatively, chloroacetylene may be formed by chloride elimination from 1,2-dichloroethenylcobalamin.[44,45]

Protonation of vinyl anions **26** and **27** presents a different pathway that may influence the ratio of **7** to **8**. Vinyl anions are generally bent species having a much larger barrier for interconversion (∼100−150 kJ/mol) than the corresponding radical, as determined both experimentally[46−49] and by computation.[50,51] The influence of chloride substitution on this barrier has been addressed by ab initio MO calculations that showed an increase of 209 kJ/mol upon chlorine substitution at the α-carbon.[52] However, chlorine substitution at the β-carbon resulted in decreases in the barrier by 64 kJ/mol for the cis position and 50 kJ/mol for the trans position. If these modulations of the barrier of the ethenyl anion are additive, then 1,2-dichloroethenyl anions **26** and **27** would have a barrier of around 300 kJ/mol, which suggests that they would not interconvert readily and the overall cis selectivity of their radical precursors would be preserved.[53,54]

Conclusions

Of the three isomeric radicals investigated in this study, the *cis*-1,2-dichloroethylene-1-yl radical (**4**) is predicted to be most stable at all computational levels. The corresponding trans isomer **5** is less stable, and the 1,1-dichloroethen-2-yl radical (**6**) is significantly less stable than **4**. The calculated geometries of these radicals suggest that stereoelectronic effects control the relative stabilities. The barrier for cis−trans interconversion between **4** and **5** is lower than that calculated for chlorinated vinyl anions, and interconversion may take place under the reaction conditions. The dominance for the formation of **4** is even more evident in chloride complexes **12**, **15**, and **17** formed after dissociative one-electron reduction of trichloroethylene (**1**). The same relative order of stability is also predicted for closed-shell products **7**−**9**, but the energy differences found for the open-shell species are much larger than those for the closed-shell products. The gas-phase barriers for O−H and C−H abstraction by radicals **4**−**6** from methanol are surprisingly similar. However, inclusion of solvent effects leads to a clear preference for C−H abstraction. These computational results explain the cis selectivity of the vitamin B_{12}-catalyzed dechlorination of TCE. The predicted reaction mechanism involves a dissociative one-electron transfer to generate 1,2-dichloroethen-1-yl radicals **4** and **5** that likely interconvert to account for the experimentally observed ratio of the *cis*- and *trans*-1,2-DCE products.

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Supporting Information Available: Structures and total energies for all stationary points at different levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) It is possible that the quantities of products derived from anions are increased by an inherent difficulty in these experiments. Once a hydrogen atom is abstracted by one of the vinyl radicals from 2-propanol, the pK_a of the hydroxyl proton in the resulting 2-propanol radical is significantly decreased (e.g., pK_a of the methanol radical is 10.6; Henglein, A. *Adv. Electroanal. Chem.* **1976**, *9*, 163), and a strongly reducing ketyl radical anion may be formed ($E° \approx -2.5$ V for the isopropyl ketyl radical anion; Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1691). This ketyl radical anion may then be the reducing agent that converts the vinyl radicals to their anions. It should be noted that the possibly artificially increased percentage of products derived from anions did not alter the high selectivity for cis products in these studies.

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(54) The individual rates of reduction of radicals **4** and **5** to their respective anions relative to the rates of their interconversion and hydrogen atom abstraction could, in principle, affect the ratio of **7** and **8** produced. Because both hydrogen atom abstraction and reduction to the anions are bimolecular processes, it is not an easy task to predict the partitioning between these two competing transformations under the various experimental conditions that have been used in the B_{12}-catalyzed dechlorination of PCE and TCE. If the cis and trans radicals have similar reduction potentials, then the high interconversion barrier for **26** and **27** maintains overall cis selectivity. However, if the reduction potential for trans radical **5** is significantly different from that for cis radical **4** *and* the reduction of the radicals to their anions is significantly faster than other transformations of these species, then the final product ratio is solely dependent on the relative reduction potentials of **4** and **5**. Such selective reduction of isomeric radicals has, in fact, been reported to determine the product ratio in the reductive dechlorination of 1,1,2,2-tetrachloroethane: Arnold, W. A.; Winget, P.; Cramer, C. J. *Environ. Sci. Technol.*, in press.

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