

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/11173868>

Reductive Dechlorination of 1,1,2,2-Tetrachloroethane

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 2002

Impact Factor: 5.33 · DOI: 10.1021/es025655+ · Source: PubMed

CITATIONS

60

READS

86

3 AUTHORS:



William A Arnold

University of Minnesota Twin Cities

119 PUBLICATIONS **3,914** CITATIONS

SEE PROFILE



Paul Winget

Georgia Institute of Technology

41 PUBLICATIONS **1,444** CITATIONS

SEE PROFILE



Christopher J Cramer

University of Minnesota Twin Cities

534 PUBLICATIONS **23,570** CITATIONS

SEE PROFILE


University of Minnesota Supercomputing Institute Research Report UMSI 2002/143

UMSI 2002/143 September 2002

**Reductive Dechlorination of
1,1,2,2-Tetrachloroethane**

**William A. Arnold, Paul Winget
and Christopher J. Cramer**

599 Walter □ 117 Pleasant St. S.E. □ Minneapolis, Minnesota 55455

 Contains a minimum 10% postconsumer waste

Reductive Dechlorination of 1,1,2,2-Tetrachloroethane

WILLIAM A. ARNOLD,^{*,†}
PAUL WINGET,^{†,§} AND
CHRISTOPHER J. CRAMER[†]

Department of Civil Engineering, University of Minnesota,
500 Pillsbury Drive SE, Minneapolis, Minnesota 55455, and
Department of Chemistry and Supercomputing Institute,
University of Minnesota, 207 Pleasant Street SE,
Minneapolis, Minnesota 55455

Products of the transformation of organic pollutants in the environment are often predicted based on the structure of the parent compounds. In some cases, however, multiple products may result from the same reaction pathway. In this study, the reduction of 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) is investigated both experimentally and computationally. Experimental results and data available in the literature reveal that the ratio of Z-1,2-dichloroethylene (Z-DCE) to E-1,2-dichloroethylene (E-DCE) produced from the reductive β -elimination of 1,1,2,2-TeCA is approximately 2:1, and this ratio is independent of the reductant used. The exception is iron metal, which results in a ratio of 4.5:1. Computational results reveal that the 1,2,2-trichloroethyl radicals (1,1,2-TCA^{*}) formed upon the transfer of the first electron are nearly isoenergetic and are in rapid equilibrium. Thus, the conformer population of the 1,1,2,2-TeCA does not dictate the product distribution. Using Marcus theory, it is demonstrated that the Z:E ratio of 2:1 reflects the relative rates of the two possible electron transfer steps to the two radical conformers. Further analysis of the thermochemistry of the reaction reveals that this ratio of rate constants should be essentially independent of the thermodynamic driving force, which is consistent with the experimental results. The different observed product distribution when iron metal is the reductant is hypothesized to result from an organometallic intermediate. The reduction of the 1,1,2,2-TeCA is an overall two-electron process, but the fact that the radicals equilibrate at a rate more rapid than the transfer of the second electron suggests that reductants employed act as decoupled single electron-transfer agents.

Introduction

The impact of a pollutant is determined not only by its persistence in the environment but also by the identities and lifetimes of any products formed via its transformation. In several cases, degradation products are known to be more toxic than the parent compound. For example, vinyl chloride, which is a known human carcinogen, is commonly observed as a product from reductive dehalogenation of the common groundwater pollutant trichloroethylene (TCE). Similarly, the moderately toxic pesticide Naled is reduced by organic thiols to form the highly toxic dichlorovos (1). Thus, it is

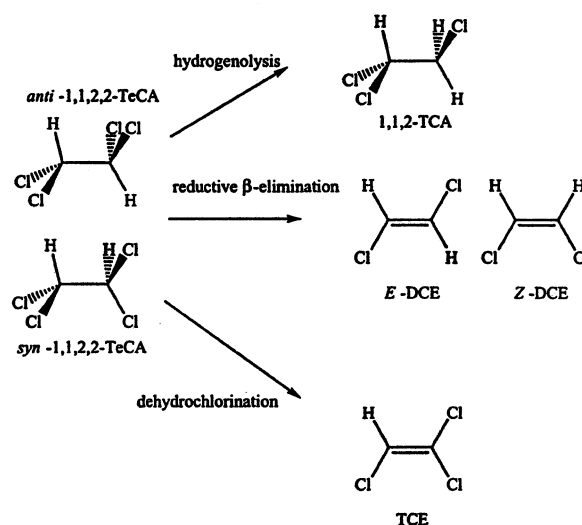


FIGURE 1. Reaction pathways of 1,1,2,2-TeCA in aquatic systems under reducing conditions.

of vital importance for environmental engineers and chemists to be able to predict not only reaction rates of environmental contaminants but also final product distributions.

Structural features often permit potential degradation products to be identified a priori. For small, halogenated alkanes, the presence of a good leaving group on a primary carbon allows nucleophilic substitution (S_N2) to take place at low activation energies. Similarly, an α - β hydrogen-halogen pair is a structural cue for elimination (E_2 , dehydrohalogenation). Small halogenated molecules are also subject to reductive processes such as hydrogenolysis (the replacement of a halogen with a hydrogen), reductive α -elimination (if geminal halogens are present), and reductive β -elimination (dihaloelimination; if vicinal halogens are present).

In many situations, however, multiple products may result from a single reaction pathway. As shown in Figure 1, the reduction of 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) may give rise to *cis*-1,2-dichloroethylene (*cis*- or Z-DCE) or *trans*-1,2-dichloroethylene (*trans*- or E-DCE) via reductive β -elimination. In addition, 1,1,2-trichloroethane (1,1,2-TCA) may result from hydrogenolysis, and TCE is the product of the dehydrochlorination reaction. The rates of reduction of the DCE isomers to vinyl chloride vary, as does the selectivity between hydrogenolysis and reductive β -elimination for these species. Thus, a method that allows the prediction of not only which products will be produced but also the relative amounts of these products would prove a useful tool for accurate assessment of the environmental impacts of organic contaminants. Computational chemistry tools have thus far proved successful in this respect (2–6).

This study focuses on the reduction of 1,1,2,2-TeCA. 1,1,2,2-Tetrachloroethane was a common solvent prior to World War II, and substantial releases have also occurred in the recent past (7, 8), leading to its detection as a groundwater contaminant. Among the chlorinated ethanes, 1,1,2,2-TeCA is unique in that the reductive β -elimination process may give rise to two products. Although the reduction of 1,1,2,2-TeCA has been studied in variety of systems, only a portion of these report product distributions (8–13). From these data, it appears that the product distribution resulting from the reductive β -elimination of 1,1,2,2-TeCA (i.e. the Z:E ratio of the resulting DCE isomers) is independent of the reducing agent employed.

* Corresponding author phone: (612)625-8582; fax: (612)626-7750; e-mail: arnol032@tc.umn.edu.

[†] Department of Civil Engineering.

[‡] Department of Chemistry and Supercomputing Institute.

[§] Present address: Computer Chemie Centrum, Nagelsbachstrasse 25 D-91025 Erlangen, Germany.

The objective of this study is to establish why the product ratio resulting from the dichloroelimination of 1,1,2,2-TeCA appears to be insensitive to the reducing agent. Additional data for the reduction of 1,1,2,2-TeCA in aqueous systems are obtained, and the product distributions are compared with previously published data. Computational chemistry methods are then used to identify the step which determines the product distribution. Theory rationalizes the observed product distributions based on the rate of transfer of the second electron in the reduction process.

Experimental Section

Chemicals. CrCl_2 (99.99%, Aldrich), CuCl (95%, Acros), 1,1,2,2-TeCA (98%, Aldrich), Z-DCE (97%, Aldrich), E-DCE (98%, Aldrich), TCE (ACS grade, Fisher), 1,1,2-TCA (97%, Aldrich), Trizma hydrochloride (Sigma), potassium iodide (Mallinckrodt), sulfuric acid (96%, Mallinckrodt), and ethylenediamine (100% anhydrous, Fisher) were used without further purification. Stock solutions of the chlorinated ethanes and ethylenes were prepared in methanol. Electrolytic Fe(0) (Fisher, 100 mesh) was acid washed as described previously (14, 15). Milli-Q water and buffer solutions were deoxygenated by sparging with purified argon.

Experimental Systems. All experiments were carried out in serum bottles (160 mL, nominal volume) sealed with Teflon faced butyl rubber septa (Chrom Tech). Reactors were prepared in an anaerobic chamber (5% H_2 :95% N_2 , Coy). Each reactor contained 100 mL of water or buffer solution with the remaining volume left as headspace. For the Cr(II) system, a CrCl_2 stock solution was diluted to the desired concentration (13 mM) with deoxygenated 5 mM sulfuric acid (pH 2) (16). At this pH, the Cr(II) exists as the hexaquo complex, and the dehydrohalogenation of the 1,1,2,2-TeCA is negligible. When Cu(I) was used as the reductant, the reactors contained a solution of 6.5 mM CuCl and 50 mM ethylenediamine prepared using deoxygenated Milli-Q water and adjusted to pH 8 using deoxygenated 1 M HCl. Reactors in which iron metal was used as the reductant contained a 50 mM pH 7 Trizma buffer (15) and a metal loading of either 0.5 or 5 g per 100 mL. When employing iodide as a reductant, an unbuffered 1 M solution of KI was used. To initiate an experiment, the reactor was spiked with the methanolic solution of 1,1,2,2-TeCA to give an initial concentration of 125–150 μM .

Analytical Methods. Headspace samples (200 μL) were withdrawn from the reactors at selected intervals after injecting an equivalent volume of purified argon. Samples were analyzed by a gas chromatograph (Trace GC, ThermoQuest) equipped with a GS-GasPro column (J&W Scientific), an FID detector, a split/splitless injector, and a PC driven data acquisition system (ChromQuest v. 2.53). Standards were prepared in serum bottles with the same air:water ratio and analyzed in an identical manner.

Computational Methods. The absolute gas-phase free energy for molecule A, $G_{\text{g},\text{A}}$, is computed as the sum of the Born–Oppenheimer electronic ground-state energy (including nuclear repulsion energy), zero-point vibrational energy, and translational, rotational, vibrational, and electronic 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) (17). The absolute free energy in aqueous solution is computed by adding to the gas-phase free energy the standard-state free energy of solvation. To convert free energies of one-electron reduction half reactions to standard reduction potentials relative to the normal hydrogen electrode (NHE), 4.44 eV is subtracted from the negative of the free energy of reaction, defined here for irreversible electron transfer as the sum of the gas-phase vertical electron attachment energy and the differential

solvation free energy of the anion product compared to the neutral radical reactant.

To compute absolute free energies, different levels of electronic structure theory were employed. All molecular geometries were optimized at the density functional level of theory. The particular functional employed was Becke's (18, 19) three-parameter exchange-correlation operator which combines exact Hartree–Fock exchange (17) with Slater's (20) local exchange functional and Becke's (21) 1988 gradient correction to Slater's functional and for correlation employs the gradient corrected correlation functional of Lee, Yang, and Parr (22). This combination is denoted B3LYP (23). 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. All these calculations employed the augmented correlation-consistent valence-triple- ζ basis set of Dunning (aug-cc-pVTZ) (24–26).

Standard-state solvation free energies in water (dielectric constant $\epsilon = 78.3$) were calculated using the SM5.42R/BPW91/DZVP aqueous solvation model (27) based on empirical atomic surface tensions and self-consistent reaction field calculations with CM2 class IV charges (28) obtained with the DZVP basis set (29); these calculations employed the gas-phase B3LYP/aug-cc-pVTZ geometries (the "R" in SM5.42R implies that the model was designed to use gas-phase geometries kept rigid in the liquid solution phase). All calculations were carried out with a locally modified version of the Gaussian 98 electronic structure program suite (30, 31).

Results and Discussion

Experimental Studies. The observed products from the reduction of 1,1,2,2-TeCA by Cr(II), Cu(I), and Fe(0) are displayed in Figure 2, along with a similar plot for Zn(0) (11). All products detected and the Z:E dichloroethylene ratios are given in Table 1. Ratios of Z:E dichloroethylene were determined by averaging the concentrations determined at each time point and by fitting the parent compound decay and product formation to a pseudo-first-order kinetic model and taking the ratio of the rate constants for the formation of the Z and E isomers. Both methods yielded statistically identical results. For Cr(II), the only observed products are Z- and E-DCE with the Z:E ratio of 2.4:1. No TCE or 1,1,2-TCA was observed. Because the Cu(I) experiment was performed at pH 8, the dehydrohalogenation process is faster than reduction, and TCE is the dominant product observed. Approximately 20% of the 1,1,2,2-TeCA is degraded via reductive β -elimination, however, with an observed Z:E ratio of the dichloroethylenes of 1.5:1. The Z:E ratio for Fe(0) is 4.5:1 at both iron loadings employed. In addition, the hydrolysis rate for the 1,1,2,2-TeCA (pH 7 half-life of ~50 days (32, 33)) is not rapid enough to account for the TCE produced over the time scale of the experiments in reactors containing either 5 g (monitored for 2.4 h) or 0.5 g (monitored over 31 h) of Fe(0). At short times, the TCE concentration exceeded that predicted from the hydrolysis rate by at least an order of magnitude. A further discussion of the Fe(0) system is provided below. Dehydrohalogenation was the only observed reaction in the 1 M KI solution.

Table 2 lists the observed products and the Z:E ratios of the dichloroethylene isomers determined by previous investigators (8–13). The Z- and E-DCE isomers resulting from dihaloelimination are generally the dominant products, and the resultant Z:E ratio ranges from 1.8:1 to 2.4:1. Also of note is that the results obtained in this work for Cr(II) and Cu(I) in water are consistent with those of Mochida et al. (9) in polar organic solvent or polar organic solvent/water mixtures. The similar values of the Z:E ratio observed for vitamin B₁₂ and hematin as reductants as well as for biotic reduction

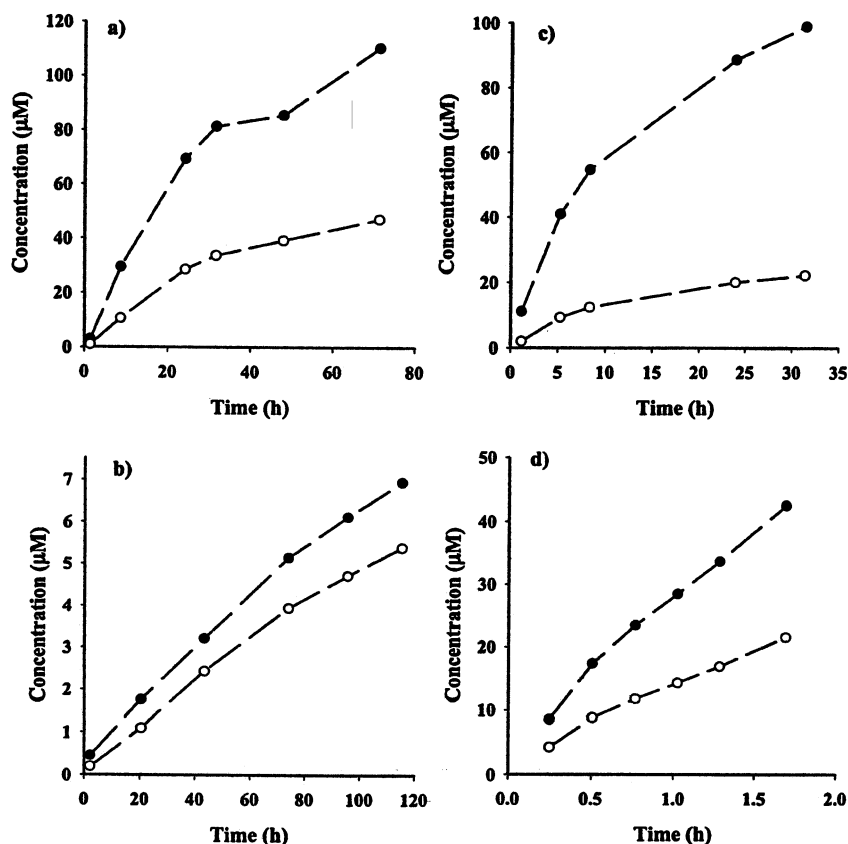


FIGURE 2. Z-DCE (●) and E-DCE (○) produced upon the reduction of 1,1,2,2-TeCA by (a) 13 mM Cr(II), (b) 6.5 mM Cu(I) with 50 mM ethylenediamine, (c) 3.1 g Fe(0)/L, and (d) 0.63 g Zn(0)/L. The data for Zn(0) is reprinted from Arnold, W. A.; Ball, W. P.; Roberts, A. L. Polychlorinated ethane reaction with zerovalent zinc: pathways and rate control. *J. Contam. Hydrol.* 1999, 40, 183–200. Copyright (1999), with permission from Elsevier Science.

TABLE 1. Results from the Reduction of 1,1,2,2-TeCA

reductant	products		C mass balance, %	ratio of Z:E 1,2-dichloroethylene
	major	minor		
Cr(II) ^a	Z-DCE, E-DCE		102	2.4 ± 0.3 ^b
Cu(I)-ethylenediamine	TCE ^c	Z-DCE, E-DCE	102	1.5 ± 0.3
Fe(0)	Z-DCE, E-DCE	TCE	98	4.5 ± 0.1
iodide	TCE		100	NA

^a This experiment was conducted at pH 2. The dehydrohalogenation product, TCE, was not observed. ^b Errors represent 95% confidence limits based on the average of the Z:E ratio determined at each time point. ^c The TCE production observed is consistent with the predicted dehydrohalogenation rate of 1,1,2,2-TeCA at pH 8.

carried out by methanogenic bacteria suggest that metal cofactors produced by the methanogens are responsible for the dechlorination of 1,1,2,2-TeCA.

One possibility to explain the nearly constant 2:1 Z:E ratio of the DCE products (excluding Fe(0)) is that the reaction is under thermodynamic control, for this ratio corresponds closely to the ratio that would be expected if the system were in thermodynamic equilibrium based on thermodynamic data (15) and our computational calculations. Experiments with E-DCE and the reductants used in this work, however, demonstrate that no equilibrium with Z-DCE is established under the various sets of experimental conditions. Reanalysis of the data from Arnold and Roberts (34) does reveal that over the time scale of days at a loading of 156 g Zn(0)/L slight conversion of E- to Z-DCE may occur, but this process would be insignificant on the time scale (<2 h) over which the reaction of 1,1,2,2-TeCA was monitored at a Zn(0) loading of 0.63 g/L.

The syn conformer of 1,1,2,2-TeCA (Figure 1), which would be expected to result in the formation of Z-DCE if dihalo-

elimination were to take place in a concerted, anti fashion, contains a dipole moment and thus should be more abundant in aqueous solution compared to the nonpolar anti-conformer. Computations predict that in water, the syn:anti ratio of 1,1,2,2-TeCA is indeed 9:1. As described below, however, this equilibrium is irrelevant to the product distribution, because all conformational information for 1,1,2,2-TeCA is lost after the first electron transfer. Moreover, the Curtin-Hammett principle indicates that product distributions should derive from relative reaction *barrier heights*, not relative equilibrium populations, unless return to equilibrium from a perturbed reactant population is much slower than are the competing reactions. We now employ theory to demonstrate that the latter situation is not applicable here, and thus the Curtin-Hammett principle holds (35).

Theoretical Studies. Reduction of alkyl halides is generally assumed to occur via a dissociative single electron transfer in which the carbon-halogen bond is cleaved resulting in the formation of an alkyl radical and a halide ion (36, 37). Initial one-electron reduction of 1,1,2,2-TeCA leads to the

TABLE 2. Literature Data of Products Observed during the Reduction of 1,1,2,2-TeCA

reductant	major products	minor products	C mass balance, %	ratio of Z/E 1,2-dichloroethylene	ref
Zn(0)	Z-DCE, E-DCE		101	1.99 ± 0.02 ^a	(17)
Cu(I)-ethylenediamine ^b	Z-DCE, E-DCE		nr ^c	2.1	(9)
Cr(II)-methyl dipropylenetriamine ^d	Z-DCE, E-DCE, 1,1,2-TCA		nr	2.1	(9)
vitamin B ₁₂ /Ti(III) citrate	Z-DCE, E-DCE	vinyl chloride, ethylene, 1,1,2-TCA	97	1.8	(10)
hematin/Ti(III) citrate	Z-DCE, E-DCE	1,1,2-TCA, TCE	84	2.2	(10)
methanogenic bacteria (live) ^e	Z-DCE, E-DCE	1,1,2-TCA, TCE	90–100	2.4 ± 0.1	(8)
methanogenic bacteria (live) ^e	Z-DCE, E-DCE	TCE, vinyl chloride, ethylene, ethane	123 ^f	2.3	(12)
methanogenic bacteria (sterilized) ^e	Z-DCE, E-DCE, TCE	vinyl chloride	119 ^f	2.1	(12)
methanogenic sediment	Z-DCE, E-DCE, 1,1,2-TCA	1,2-DCA	nr	3.2 ^g	(13)

^a If multiple observations or data points were reported, the average and 95% confidence limits are shown. ^b Solvent used was 1:1 dimethyl sulfoxide:methanol. ^c Not reported. ^d Solvent used was 1:1 dimethyl sulfoxide:water. ^e Bacteria obtained from municipal sludge reactors. ^f Mass balances for 1,1,2,2-TeCA systems are consistently high in ref 12, suggesting a miscalculation of the initial mass added. ^g The Z-DCE and E-DCE did react in this system, and this may influence the reported ratio.

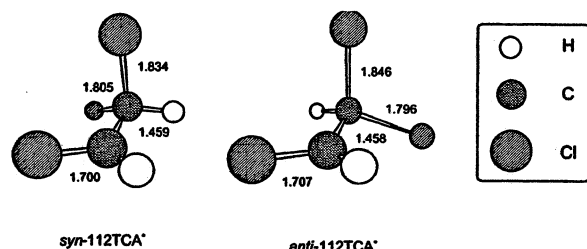


FIGURE 3. Geometries of syn and anti 1,1,2-TCA* optimized at the B3LYP/aug-cc-pVTZ level. Heavy-atom bond distances (Å) are shown.

1,1,2-trichloroethyl radical (1,1,2-TCA*). Theory indicates that this radical has two conformational minima, shown in Figure 3, each of which is 2-fold degenerate. Each conformer eclipses the half-filled orbital of the radical center with a C(2)-Cl bond, thereby maximizing hyperconjugation (38); the difference between them is that in one case the other C(2)-Cl bond is syn to the Cl on C(1) (syn-1,1,2-TCA*), while in the second case it is anti to it (anti-1,1,2-TCA*). The eclipsing C(2)-Cl bond is 0.04–0.05 Å longer than the noneclipsing one, consistent with invocation of hyperconjugation.

Computationally, electron attachment to either the syn or the anti rotamers of 1,1,2-TCA* leads to spontaneous ejection of the chloride involved in the eclipsing bond of the radical. Thus, one possible explanation for the highly conserved 2:1 Z:E ratio of the 1,2-dichloroethylene products would be that the intermediate radicals are formed in a 2:1 syn:anti ratio, and that this ratio does not interconvert on the time scale of the second electron transfer. A similar explanation was proposed previously to explain the Z:E ratio resulting from the reduction of 1,1,2,2-TeCA by Cr(II) and Cu(I) complexes (9). Theory suggests, however, that this explanation cannot be valid. Our results show that several different levels of electronic structure theory all agree that in aqueous solution the two radicals are essentially iso-energetic and thus should be present in nearly equivalent amounts—our best level of theory, described in the methods section, predicts a free energy difference of 0.02 kcal mol⁻¹. Furthermore, the rotational barrier for their interconversion is predicted to be about 3.5 kcal mol⁻¹. At 298 K, the rate constant for a unimolecular process having an activation free energy of 3.5 kcal mol⁻¹ is roughly 10¹⁰ s⁻¹ (39). Thus, the two radicals are in rapid equilibrium.

Because the product 1,2-dichloroethylenes do not interconvert under the reaction conditions and insofar as computations suggest that there are no anionic intermediates following electron transfer to 1,1,2-TCA*, the observed product ratio must reflect the relative rates of the two possible electron-transfer steps. To compute this relative rate, we make

use of Marcus theory (40, 41). Although Marcus theory should only apply to outer-sphere electron transfer, it has been demonstrated that Marcus theory can explain reactivity trends for reductants that have inner-sphere character as well (42–44). In its simplest derivation, Marcus theory indicates that the electron-transfer rate constant may be computed as

$$k_{ET} = Z e^{-(\Delta G^\circ + \lambda)^2/4\lambda RT} \quad (1)$$

where Z is the collision frequency between redox partners, ΔG° is the overall free energy change for the equilibrium redox process, λ is the so-called reorganization energy, R is the universal gas constant, and T is temperature. As we are interested in a ratio of rates, we may write

$$\frac{k_{ET}(\text{syn})}{k_{ET}(\text{anti})} = \frac{Z_{\text{syn}} e^{-(\Delta G_{\text{syn}}^\circ + \lambda_{\text{syn}})^2/4\lambda_{\text{syn}} RT}}{Z_{\text{anti}} e^{-(\Delta G_{\text{anti}}^\circ + \lambda_{\text{anti}})^2/4\lambda_{\text{anti}} RT}} \quad (2)$$

Insofar as the reactants differ only as conformers, we may assume that Z and λ are identical for the two systems, leading to

$$\frac{k_{ET}(\text{syn})}{k_{ET}(\text{anti})} = e^{-[(\Delta G_{\text{syn}}^\circ + \lambda)^2 - (\Delta G_{\text{anti}}^\circ + \lambda)^2]/4\lambda RT} \quad (3)$$

We may use theory to evaluate the free energy change ΔG° for the electron attachment to 1,1,2-TCA*. Some approximations, however, must be made in the process. In this case, we take the free energy change as the sum of the gas-phase vertical electron affinity (–31.9 kcal mol⁻¹ for syn and –30.9 kcal mol⁻¹ for anti) and the equilibrium solvation free energy difference between the frozen-geometry anion and its antecedent radical (–50.2 kcal mol⁻¹ for syn and –50.5 kcal mol⁻¹ for anti). Relative to the NHE, the corresponding half reactions thus have standard reduction potentials of –0.88 and –0.91 V, respectively. These reduction potentials may be used in combination with the standard potentials of the reducing agents to compute the overall driving force. Table 3 shows the Z:E ratios predicted from eq 3 for different standard reduction potentials ranging from –0.2 to –1.0 V, which effectively spans the experimental range examined here. The results are presented for three different choices of the reorganization energy λ . The lowest reorganization energy, 50 kcal mol⁻¹, is in the range of what would be expected for an electron transfer between neutral and anionic partners the size of 1,1,2-TCA*, while the larger reorganization energies are in the range of what might be expected from highly charged, small metal ions acting as reductants (41). (Note that the “equilibrium” free energy change is predicted to be positive for the weaker reducing agents, but that is

TABLE 3. Ratio of Z:E 1,2-Dichloroethylene Predicted from Eq 3 for Different Reducing Agent Reduction Potentials and Reorganization Energies

reduction potential, V	$\Delta G_{\text{syn}}^{\circ}$ kcal mol ⁻¹	$\Delta G_{\text{anti}}^{\circ}$ kcal mol ⁻¹	$k_{\text{ET}}(\text{syn})/k_{\text{ET}}(\text{anti})$		
			$\lambda = 50 \text{ kcal mol}^{-1}$	$\lambda = 75 \text{ kcal mol}^{-1}$	$\lambda = 100 \text{ kcal mol}^{-1}$
-1.0	-2.8	-2.1	1.68	1.70	1.71
-0.8	1.8	2.5	1.77	1.76	1.75
-0.6	6.5	7.1	1.86	1.82	1.79
-0.4	11.1	11.7	1.96	1.88	1.84
-0.2	16.3	15.7	2.06	1.94	1.89

because the strongly exergonic dissociation of chloride ion, which drives the reaction even with the weaker reducing agents, is not accounted for here in the kinetics of the electron-transfer step.)

The Marcus theory predictions are found to be in remarkably good agreement with the observed 2:1 Z:E ratio and are furthermore consistent with experiment in predicting this ratio to be largely insensitive to the standard reduction potential of the reductant over the range of -0.2 to -1.0 V. The theory predicts that sensitivity of the product ratio to the reducing agent decreases with increasing reorganization energy. This insensitivity can be rationalized by manipulating eq 3. If we take

$$\delta = \Delta G_{\text{anti}}^{\circ} - \Delta G_{\text{syn}}^{\circ} \quad (4)$$

then one can rewrite eq 3 as

$$\frac{k_{\text{ET}}(\text{syn})}{k_{\text{ET}}(\text{anti})} = e^{-\delta(2\Delta G_{\text{syn}}^{\circ} - \delta - 2\lambda)/4\lambda RT} \quad (5)$$

When the driving force ΔG° and δ are small compared to λ , as is the case here, this equation further simplifies to

$$\frac{k_{\text{ET}}(\text{syn})}{k_{\text{ET}}(\text{anti})} = e^{\delta/2RT} \quad (6)$$

which is independent of absolute driving force and thus of reducing agent. This equation also suggests that the ratio is dependent only on the relative (rather than the absolute) values of ΔG° for the two radical species. Given the value for δ noted above (0.03 eV or 0.7 kcal mol⁻¹), eq 6 predicts a ratio of somewhat less than 2:1 at 298 K, as seen in Table 3.

Mechanistic Interpretations and Environmental Significance. A previous study by Totten et al. (16) used vicinal dibromides to analyze the dihaloelimination process with a variety of reducing agents. These investigators observed that reduction by four zerovalent metals (Zn, Cu, Al, Fe) and ferrous iron sorbed to goethite (α -FeOOH) resulted in Z:E ratios comparable to the nucleophilic ("two-electron") reductant iodide and markedly different from the one-electron reductant Cr(II). The authors noted that they were unable to determine whether the reduction process was proceeding via a two-electron transfer of halonium ion or a single-electron transfer (SET) mechanism, for if the second electron is transferred faster than carbon-carbon bond rotation, it would appear to be a "two-electron" process. The results from the present work and those available in the literature reveal that the product distributions resulting from the dihaloelimination of 1,1,2,2-TeCA by all reductants tested (with the exception of Fe(0)) give Z:E ratios comparable to that observed for Cr(II), suggesting that the SET mechanism is operational in the reduction of 1,1,2,2-TeCA. This indicates that, at least for chlorinated alkanes, zerovalent metals as well as metal-containing cofactors act as one-electron-transfer agents and that the product distribution is determined by the relative rate constants of any radical species in equilibrium via C-C bond rotation.

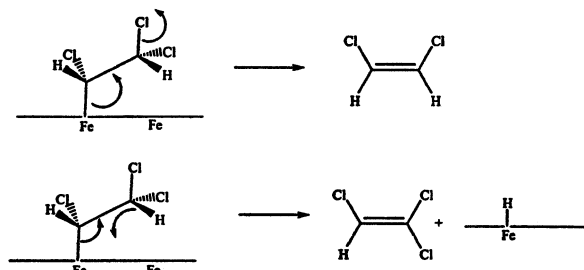


FIGURE 4. Hypothesized surface reaction mechanism for 1,1,2,2-TeCA at an electron rich Fe atom on an iron metal or iron oxide coated surface.

The computational results also allow refinement of the estimation of the rate of second electron transfer. Based on the rotational barrier for the alkyl bromide radicals, Totten et al. estimated that the second electron transfer would have a rate constant faster than 10⁹ s⁻¹ to explain the observed product distributions if the two intermediate radicals were reduced at the same rate (16). The carbon-carbon bond rotation rate constant for 1,1,2,2-TeCA is approximately 10¹⁰ s⁻¹, and because the calculations suggest that the radicals must equilibrate prior to the second-electron transfer to explain the observed product distribution, the rate constant for transfer of the second electron must be less than this value.

The 4.5:1 Z:E ratio observed with iron also requires further examination. Based on the potential (-0.44 V vs NHE) of the Fe²⁺ + 2e⁻ → Fe(0) reaction, the Z:E ratio should be between 1.84 and 1.96 depending on the reorganization energy (Table 3). The potential of the iron half reaction in the experimental systems is certainly more negative than the standard value, which would lead to a slightly lower predicted Z:E ratio (Table 3). The excess Z isomer cannot be the result of the reduction of the TCE observed as a product. First, TCE predominantly reacts via reductive β -elimination to form chloroacetylene under the experimental conditions employed (15), and the Z:E ratio of the DCE isomers observed from the reduction of TCE is approximately 1.5:1. Also, the Z and E isomers of DCE react with Fe(0) at nearly identical rates under these conditions (15), and thus the excess Z-DCE cannot be explained by more rapid reaction of E-DCE with Fe(0). The possibility that the transfer of the second electron from iron metal is faster the equilibration of the 1,1,2-TeCA[•] cannot entirely be eliminated. Results measuring the second-electron-transfer rate using radical clocks, however, indicate that the rate of transfer of the second electron from iron is slower than for other reductants (44).

The excess formation of the Z isomer may result from the 1,1,2,2-TeCA being constrained at the iron surface in the form of an organometallic intermediate. This intermediate would then control the product distribution. Arnold and Roberts (15) proposed that metal-carbon bonds form during the reduction of chlorinated ethylenes by Fe(0). A similar proposed intermediate is shown for 1,1,2,2-TeCA in Figure 4. The trichloroethyl group is thought to be bound through a single Fe-C covalent bond and thus is bound differently

than substituted ethylenes which bind through their π orbitals. If the chlorine atoms are somehow constrained as depicted, the Z isomer would be expected to dominate. This hypothesized intermediate may also explain the production of TCE observed, which is faster than the rate predicted by the dehydrohalogenation of 1,1,2,2-TeCA at the pH employed. If a hydrogen is transferred to the iron metal center on the metal or oxide surface from the trichloroalkyl complex as shown, the resulting elimination-type product would be TCE (Figure 4). This β -elimination reaction is a known decomposition pathway of organometallic species containing iron-carbon σ -bonds (45, 46). It cannot be ruled out, however, that the reduction of water near the iron surface results in localized increased concentration of hydroxide that leads to more rapid dehydrohalogenation. Further investigations are necessary to completely explain the experimental observations in the Fe(0) system.

Initial structural analysis of environmental contaminants can give potential products, but identifying actual products requires experimental studies. Even then, elucidating the product determining step of a reaction can be elusive. Computational chemistry methods are useful to the extent that various alternative possibilities can be evaluated, and the results presented herein demonstrate that computational methods can be useful in rationalizing (and, in principle, predicting) product distributions when multiple products may result from a single reaction. This work also reveals that the product distribution resulting from the reduction of 1,1,2,2-TeCA (and potentially other chlorinated alkanes) is not dictated by the conformer population of the parent compound or of any intermediate radical species but rather by the relative reduction rates of the radicals that form. We expect future combinations of experimental and computational studies to prove effective in the prediction of both transformation rates and product distributions for organic contaminants in environmentally relevant systems.

Acknowledgments

The authors wish to thank Kristopher McNeill for helpful discussions regarding the results with Fe(0) and Lisa Totten for preliminary review of the manuscript. The comments from the anonymous reviewers were very helpful. C.J.C. thanks the National Science Foundation for financial support (CHE-9876792).

Literature Cited

- (1) Scheybal, A.; Gabro, T.; Konrad, H. Z. *Chem.* **1978**, *18*(11), 404–405.
- (2) Barrows, S. E.; Cramer, C. J.; Truhlar, D. G.; Weber, E. J.; Elovitz, M. S. *Environ. Sci. Technol.* **1996**, *30*, 3028–3038 (erratum, **1997**, *31*, 612).
- (3) Scherer, M. M.; Balko, B. A.; Gallagher, D. A.; Tratnyek, P. G. *Environ. Sci. Technol.* **1998**, *32*, 3026–3033.
- (4) Lim, M.; Cramer, C. J. *J. Phys. Org. Chem.* **1998**, *11*, 149–154.
- (5) Butler, E. C. *ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.* **2000**, *40*(1), 325–327.
- (6) Patterson, E. V.; Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 2025–2031.
- (7) *1991 Toxics Release Inventory-Public Data Release*; United States Environmental Protection Agency, Office of Pollution Prevention and Toxics: Washington, DC, 1991.
- (8) Chen, C.; Puhakka, J. A.; Ferguson, J. F. *Environ. Sci. Technol.* **1996**, *30*(2), 542–547.
- (9) Mochida, I.; Noguchi, H.; Fujitsu, H.; Seiyama, T.; Takeshita, K. *Can. J. Chem.* **1977**, *55*, 2420–2425.
- (10) Schanke, C. A.; Wackett, L. P. *Environ. Sci. Technol.* **1992**, *26*(4), 830–833.
- (11) Arnold, W. A.; Ball, W. P.; Roberts, A. L. *J. Contam. Hydrol.* **1999**, *40*(1–2), 183–200.
- (12) van Eekert, M. H. A.; Stams, A. J. M.; Field, J. A.; Schraa, G. *Appl. Microbiol. Biotechnol.* **1999**, *51*, 46–56.
- (13) Lorah, M. M.; Olsen, L. D. *Environ. Sci. Technol.* **1999**, *33*(2), 227–234.
- (14) Fennelly, J. P.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*(13), 1980–88.
- (15) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **2000**, *34*(9), 1794–1805.
- (16) Totten, L. A.; Jans, U.; Roberts, A. L. *Environ. Sci. Technol.* **2001**, *35*(11), 2268–2274.
- (17) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; Wiley: Chichester, 2002.
- (18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (19) Stephens, P. J.; Devlin, F. J.; Ashwar, C. S.; Bak, K. L.; Taylor, P. R.; Frisch, M. J. Comparison of Local, Nonlocal, and Hybrid Density Functionals Using Vibrational Absorption and Circular Dichroism Spectroscopy. In *Chemical Applications of Density Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; American Chemical Society: Washington, DC, 1996; pp 105–113.
- (20) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.
- (21) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3111.
- (22) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–798.
- (23) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (24) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (25) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.
- (26) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*(2), 1358–1371.
- (27) Zhu, T.; Li, J.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *J. Chem. Phys.* **1998**, *109*, 9117–9133.
- (28) Li, J.; Zhu, T.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **1998**, *102*, 1820–1831.
- (29) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–583.
- (30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98 (Revision A.10)*; Gaussian, Inc.: Pittsburgh, PA, 2001.
- (31) Xidos, J. D.; Li, J.; Thompson, J. D.; Hawkins, G. D.; Winget, P. D.; Zhu, T.; Rinaldi, D.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G.; Frisch, M. J. *MN-GSM version 1.8*; University of Minnesota: Minneapolis, MN, 2001.
- (32) Hagg, W. R.; Mill, T. *Environ. Sci. Technol.* **1988**, *22*(6), 658–663.
- (33) Jeffers, P. M.; Ward, L. M.; Woytowitch, L. M.; Wolfe, N. L. *Environ. Sci. Technol.* **1989**, *23*(8), 965–969.
- (34) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*(16), 3017–3025.
- (35) Curtin, D. Y. *Recent Chem. Prog.* **1954**, *15*, 111–165.
- (36) Eberson, L. *Acta Chem. Scand.* **1999**, *53*, 751–764.
- (37) Totten, L. A.; Roberts, A. L. *Crit. Rev. Environ. Sci. Technol.* **2001**, *31*(2), 175–221.
- (38) Cramer, C. J. *J. Mol. Struct.: THEOCHEM* **1996**, *370*, 135–146.
- (39) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*, 2nd ed.; Prentice Hall: New York, 1999.
- (40) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*(5), 966–978.
- (41) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001; pp 117–124.
- (42) Eberson, L. *Acta Chem. Scand. B* **1982**, *36*, 533–543.
- (43) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987.
- (44) Totten, L. A. Ph.D. Thesis. *The use of model and probe compounds to investigate the mechanisms of reductive dehalogenation reactions*; The Johns Hopkins University: Baltimore, MD, 1999.
- (45) Bowden, F. L.; Wood, L. H. Compounds with Iron-Carbon σ -Bonds. In *The Organic Chemistry of Iron-Volume I*; Von Gustof, E. A. K., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1978; pp 345–396.
- (46) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*; VCH Verlagsgesellschaft mbH: Weinheim, Germany, 1989; pp 193–205.

Received for review March 15, 2002. Revised manuscript received May 23, 2002. Accepted May 29, 2002.

ES025655+