

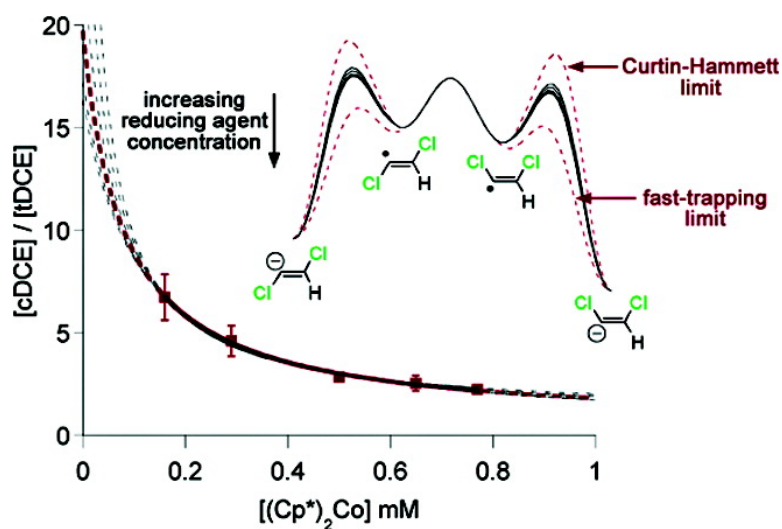
Communication

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J. Am. Chem. Soc., **2005**, 127 (3), 844-845 • DOI: 10.1021/ja043569z • Publication Date (Web): 31 December 2004

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Reduction of Trichloroethylene by Outer-Sphere Electron-Transfer Agents

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Trichloroethylene (TCE) is a widely used industrial solvent that contaminates many groundwater and soil environments.¹ Vitamin B₁₂ has been found to function as a catalyst in the dechlorination of TCE and may have applications in the remediation of contaminated sites.^{2–6} Although the process of dechlorination with B₁₂ has been studied by many authors, the mechanism is not established. One of the major points of uncertainty is the degree to which the reduction of TCE proceeds through an outer-sphere electron-transfer mechanism.^{2,4,5,7} The product distribution is one indication that a non-outer-sphere reduction process may be operating. Stereochemical product ratios have been used in other systems to distinguish between outer-sphere and non-outer-sphere electron-transfer mechanisms.⁸ In the reduction of TCE by B₁₂, the ratio of *cis*-dichloroethylene (cDCE) to *trans*-dichloroethylene (tDCE) is high (about 23:1),^{3,5,9} which is significantly different than the ratio one would expect based on the relative stabilities of the DCEs (3:1) and the likely intermediate vinyl radicals (4–6:1).¹⁰ In this work, we examine whether the [cDCE]:[tDCE] ratio can be used as a diagnostic of the mechanism.

A series of well-characterized outer-sphere electron-transfer agents composed of both aromatic radical anions and cobaltocenes were used to explore the reduction of TCE. The radical anions of naphthalene (C₁₀H₈^{•-}, *E*_{1/2} = -2.28 V),^{11–13} pyrene (C₁₆H₁₀^{•-}, *E*_{1/2} = -1.81 V),^{11–14} and perylene (C₂₀H₁₂^{•-}, *E*_{1/2} = -1.42 V),^{11,12,14,15} offer a range of reduction potentials¹⁶ with well-studied behavior.^{12,17} The second class of reducing agents, decamethylcobaltocene (Cp*₂Co, *E*_{1/2} = -1.22 V)¹⁸ and cobaltocene (Cp₂Co, *E*_{1/2} = -0.64 V),^{12,18,19} was chosen because the agents are well-characterized cobalt-centered reductants and because of the similarity of cobaltocene's reduction potential to that of the vitamin B₁₂ Co^I/Co^{II} couple (*E*_{1/2} = -0.58 V).²⁰

Reduction experiments were performed under nitrogen atmosphere using dry solvents in sealed tube reaction vessels to prevent volatilization of substrate or products. A solution of reducing agent was added dropwise to a solution of TCE (2 mM) to give a final concentration of 0.5 mM reducing agent. At the completion of the reaction, samples were analyzed by GC–MS.

In all cases, the same four products were observed: cDCE, tDCE, dichloroacetylene, and chloroacetylene (see Supporting Information for full product distribution details). The focus of this study was the ratio of [cDCE] to [tDCE], and a summary of the experimental results can be seen in Figure 1. For a given reducing agent, there is variation in the [cDCE]:[tDCE] product ratio in different solvents. Over the reduction potential range, the [cDCE]:[tDCE] ratio varied from 0.87 to 4.5, and an empirical, rough linear free-energy relationship (LFER) is seen with higher ratios observed for weaker reductants (Figure 1).

Most of the published work on TCE reduction by vitamin B₁₂ has been conducted in water at catalytic concentrations of B₁₂ in the presence of a bulk reductant, such as titanium (III) citrate.^{2,3,5,21} To maintain consistent conditions used in the present study and to alleviate any interference by a bulk electron source, a solution of

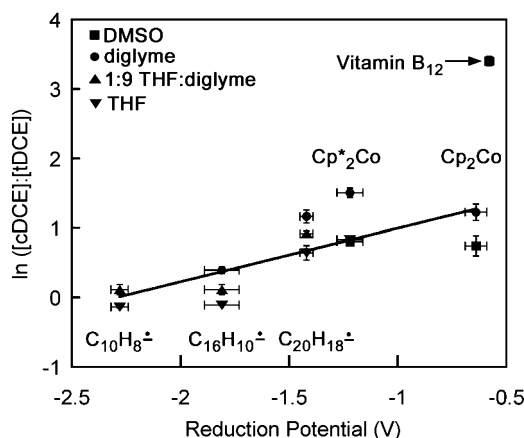
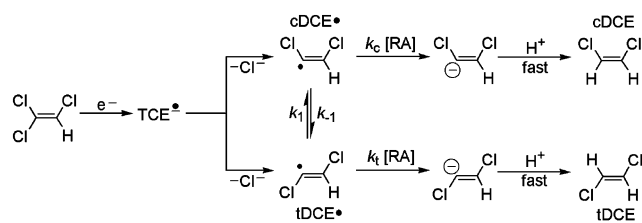


Figure 1. Observed ln [cDCE]:[tDCE] ratio versus reduction potential for the reduction of TCE by outer-sphere reducing agents and vitamin B₁₂ in various solvents. The line fit incorporates outer-sphere electron-transfer agents in all solvents. Y-error bars are the standard deviation of triplicate experiments; X-error bars illustrate the standard deviation in the literature values for reduction potential in various solvents;^{12–21} error bars are shown or contained within the symbol.

vitamin B₁₂ (Co(I)) in DMSO was prepared through reduction by zinc amalgam²² and was used to reduce TCE in a stoichiometric fashion. The same four reduction products were observed as those for the outer-sphere electron-transfer agents, but in this case, the [cDCE]:[tDCE] ratio was 30:1. When this ratio is compared to that of the other reductants (Figure 1), it is evident that vitamin B₁₂ does not fit the trend observed for the outer-sphere reductants. This conclusion is consistent with the hypothesis that the reduction of TCE by vitamin B₁₂ occurs through a non-outer-sphere electron-transfer mechanism and may include the formation of organo-cobalamin intermediates.^{2,4,7,21,23}

A reaction sequence was proposed to account for the dependence of the [cDCE]:[tDCE] ratio on the strength of reducing agent (RA) (Scheme 1). This scheme is similar to that put forth by Nonnenberg et al. to summarize their theoretical results on the reduction of TCE and includes the intermediacy of the TCE π* anion radical, as suggested by Costentin et al.^{10,24} With the addition of a single electron, the resulting TCE radical anion is unstable and ejects chloride to produce an initial distribution of *cis*-dichlorovinyl radical (cDCE*) and *trans*-dichlorovinyl radical (tDCE*).^{5,10} In this mechanism, the inversion rate for these radicals is competitive with

Scheme 1



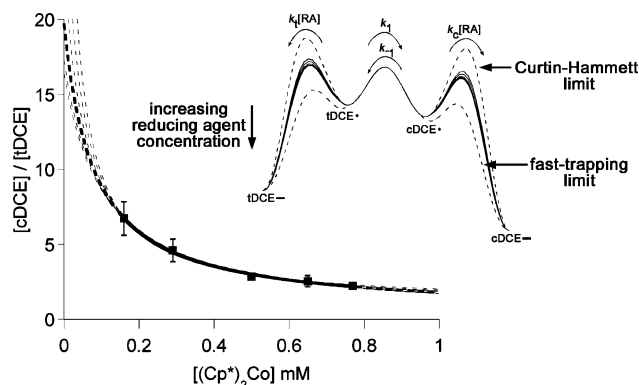


Figure 2. Effect of varying $[\text{Cp}^*_2\text{Co}]$ on the final product ratio in the reduction of TCE. Data were fit to eq 1. The series of curve-fits correspond to $[\text{cDCE}]_i:[\text{tDCE}]_i$ values ranging from 0.1 to 1.0. The bold line corresponds to $[\text{cDCE}]_i:[\text{tDCE}]_i = 0.4$. Error bars are the standard deviation of triplicate experiments. The potential-energy diagram illustrates the relative barrier heights as calculated from the family of curve-fits. The dashed lines are estimated extremes of reducing agent concentration ($[\text{RA}] = 1 \mu\text{M}$ and 100 mM).

further reduction to the stereochemically rigid vinyl anions. The vinyl radicals can isomerize with relative ease; the barrier to inversion has been calculated to be 6–9 kcal/mol, while the anions have an inversion barrier of ~ 72 kcal/mol and can, therefore, be considered stereochemically stable.¹⁰ The final product ratio formed from the initial distribution of cDCE^* and tDCE^* , and its dependence on reducing agent concentration, is given by eq 1, where $[\text{cDCE}]_i$ and $[\text{tDCE}]_i$ represent the initial concentrations of cDCE^* and tDCE^* , respectively (see Supporting Information for the derivation of this equation). Two important limits are the Curtin–Hammett limit (eq 2) and the fast-trapping limit (eq 3), which correspond to low $[\text{RA}]$ and high $[\text{RA}]$, respectively.

$$\frac{[\text{cDCE}]}{[\text{tDCE}]} = \frac{\left(\frac{k_c}{k_{-1}} \right) \left(\frac{k_t[\text{cDCE}^*]_i}{k_1[\text{tDCE}^*]_i} [\text{RA}] + \frac{[\text{cDCE}^*]_i}{[\text{tDCE}^*]_i} + 1 \right)}{\left(\frac{k_c}{k_{-1}} \right) \left(\frac{k_t[\text{tDCE}^*]_i}{k_1[\text{cDCE}^*]_i} [\text{RA}] + \frac{[\text{tDCE}^*]_i}{[\text{cDCE}^*]_i} + 1 \right)} \quad (1)$$

$$\lim_{[\text{RA}] \rightarrow 0} \frac{[\text{cDCE}]}{[\text{tDCE}]} = \frac{k_c k_1}{k_t k_{-1}} \quad (2)$$

$$\lim_{[\text{RA}] \rightarrow \infty} \frac{[\text{cDCE}]}{[\text{tDCE}]} = \frac{[\text{cDCE}^*]_i}{[\text{tDCE}^*]_i} \quad (3)$$

This mechanism was tested by examining the effect of reducing agent concentration on the final $[\text{cDCE}]:[\text{tDCE}]$ ratio and was studied using Cp^*_2Co in DMSO. Reaction conditions were followed as described above with a range of reductant concentrations from 0.16 to 0.77 mM. The results of these experiments are shown in Figure 2. Lower reducing agent concentrations result in higher $[\text{cDCE}]:[\text{tDCE}]$ ratios, which is consistent with the radical intermediates having longer to equilibrate toward the more stable cDCE^* .¹⁰

Equation 1 describes the data quite well, although the Curtin–Hammett region of the curve is not well-defined. Obtaining data points at low $[\text{Cp}^*_2\text{Co}]$ was difficult due to a lack of analytical sensitivity in determining product ratios at low reducing agent concentration. The data were fit to a family of curves by setting values of $[\text{cDCE}]_i:[\text{tDCE}]_i$ between 0.1 and 1. At $[\text{cDCE}]_i:[\text{tDCE}]_i$

$= 0.4$ (the bold fit in Figure 2), ratios of the rate constants, $k_t/k_{-1} = 0.90 \text{ M}^{-1}$ and $k_c/k_{-1} = 18 \text{ M}^{-1}$, were calculated.

This work establishes that outer-sphere reduction of TCE leads to $[\text{cDCE}]:[\text{tDCE}]$ ratios of less than 5:1 and thus provides a basis for the use of this product ratio as a diagnostic for the mechanism of TCE reduction. We conclude that outer-sphere reduction of TCE by vitamin B_{12} is unlikely to be the major pathway.

Acknowledgment. This work was supported by the National Science Foundation (CHE-0239461). We thank Professor Christopher Cramer and Ms. Elizabeth Stone for their helpful discussions and work with calculations.

Supporting Information Available: Full experimental details, product distribution data, and the derivation of eq 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA043569Z