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Communication

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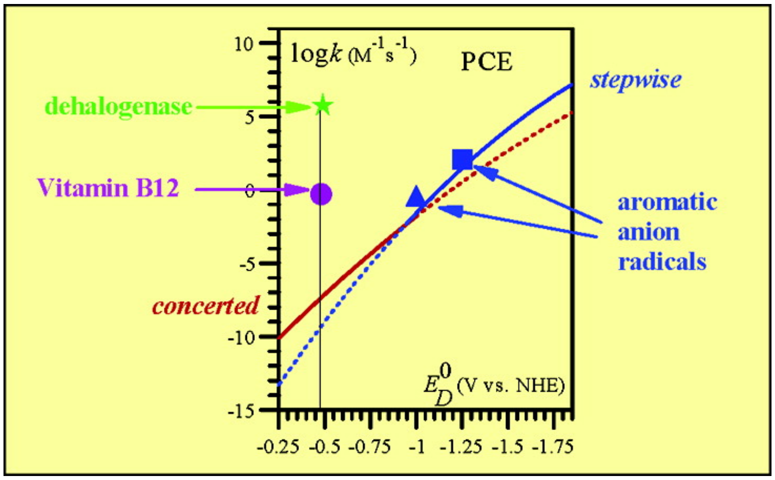

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Does Catalysis of Reductive Dechlorination of Tetra- and Trichloroethylenes by Vitamin B12 and Corrinoid-Based Dehalogenases Follow an Electron Transfer Mechanism?

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Tetrachloroethylene ("perchloroethylene", PCE) and trichloroethylene (TCE) are particularly dangerous members of the vast class of organic chloride pollutants.[1] Reductive cleavage of these two compounds, notably, by means of low-valent vitamin B12 or analogous corrinoids, currently attracts active attention for two motives. One is to provide information that may serve as a basis for establishing remediation strategies. The other interesting issue concerns the implication of low-valent cobalamin and other cobalt corrinoids in the enzymatic reduction of PCE and TCE by several anaerobic bacteria in the framework of a dehalorespiration process.[2] In both cases, an important mechanistic question is the nature of the first and rate-determining step of the reaction. On the basis of kinetic, spectroscopic, and deuteration experiments, an electron transfer mechanism has been suggested for this initial step;[3] one electron is transferred from the Co(I) corrinoid to the chloro compound accompanied by the cleavage of a carbon halogen bond, thus yielding the corresponding vinyl radical and chloride ion. The vinyl radical is eventually reduced by means of a second electron transfer into the carbanion and ultimately yields, after protonation, the hydrogenolysis product. This mechanism does not seem to match stereochemical evidence recently gained in the case of TCE.[4] It also differs from the mechanism proposed for corrinoid-based dehalogenase reductions, which suggests the formation of a cobalt (tri- or dichlorovinyl) intermediate as the initial step.[2b,h,i]

We have found that it is possible to decide on kinetic basis whether the electron transfer mechanism is operative or not. Figure 1 delineates, in terms of potential energy profiles, the dichotomy and competition between stepwise and concerted mechanisms for electron transfer/bond breaking reactions.[5] It is also necessary to take into account the fact that non-negligible interactions may exist between the caged fragments, even in a polar solvent, leading to a σ anion radical rather than to two independent species.[6,7] Consideration of the latter factor is particularly important in the present cases in view of the strong electron-withdrawing effect exerted by the chlorine atoms in the tri- or dichlorovinyl radicals, as illustrated previously by other radicals bearing electron-withdrawing groups.[6a,c,7]

If the initial electron transfer is the rate-determining step of the stepwise process (which is the case of interest here), the two pathways are characterized by activation/driving force relationships that are formally the same:

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \tag{1}$$

$$\alpha = 0.5\left(1 + \frac{\Delta G^0}{\lambda}\right) = \sqrt{\frac{\Delta G^{\ddagger}}{\lambda}} \tag{2}$$

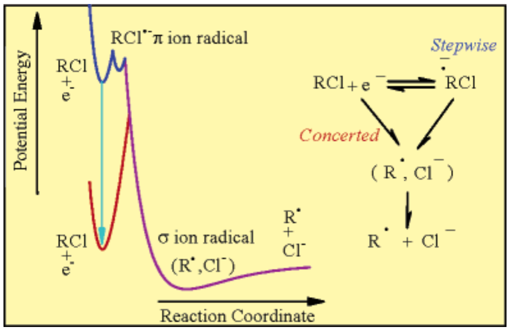

Figure 1. Heterogeneous (electrochemical) or homogeneous reductive cleavage of an organic chloride (such as PCE and TCE) by an outersphere electron donor. Potential energy profiles showing the dichotomy and transition between stepwise and concerted electron transfer/bond breaking pathways.

Table 1. Parameters for the Concerted and Stepwise Pathways in the Electrochemical Reduction[a] of PCE and TCE[b]

pathway	concerted			stepwise			
compound	$E^0_{\mathrm{RX/R^\bullet + X^-}}$	D_R	D_CF	$E^0_{\mathrm{RX/RX^{\bullet -}}}$	a^c	λ^{el}	λ_i^d
PCE	−1.334	3.80	0.370	−1.71	3.44	1.65	0.78
TCE	−1.460	3.88	0.345	−1.94	3.29	1.68	0.75

[a] In DMF at 25 °C. [b] Energies in eV, potential in V vs NHE. [c] Radius of the equivalent hard sphere in Å. [d] Intramolecular reorganization energy estimated from application of eq 4, in this case: $\lambda^{\mathrm{el}} = \lambda_0^{\mathrm{el}} + \lambda_i$ and $\lambda_0^{\mathrm{el}}(\mathrm{eV}) = 3/a(\mathrm{Å})$.[7]

$\Delta G^{\ddagger}$ is the activation free energy, and α is the transfer coefficient (symmetry factor); $\Delta G^\circ = E - E^\circ$.[8] E° is the standard potential. E is the electrode potential in the electrochemical case. It is equal to E°_D, the standard potential of the donor couple in the case of a homogeneous reaction. The standard potentials and reorganization energies are not the same for the two pathways.[5]

In the stepwise case

$$E^0 = E^0_{\mathrm{RCl/RCl^{\bullet -}}} \text{ and } \lambda = \lambda_0 + \lambda_i \tag{3}$$

(λ_0 and λ_i are the solvent and intramolecular reorganization energies, respectively).

In the concerted case

$$E^0 = E^0_{\mathrm{RCl/R^\bullet + Cl^-}} \text{ and } \lambda = \lambda_0 + (\sqrt{D_\mathrm{R}} - \sqrt{D_\mathrm{CF}})^2 \tag{4}$$

where D_R is the RCl homolytic bond dissociation energy of the reactant, whereas D_CF measures the attractive interaction between the caged fragments.[6]

Previous electrochemical measurements[7] and estimation of the pertinent thermodynamic parameters provided the values summarized in Table 1 as elements for the distinction between the two pathways. It was concluded that the electrochemical reaction follows the stepwise pathway rather than the concerted pathway because

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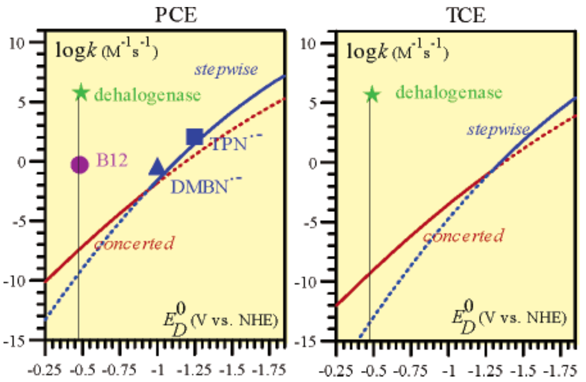

Figure 2. Homogeneous reductive cleavage of PCE and TCE by outersphere electron donors. Activation/driving force plots for the stepwise (blue line) and concerted (red line) electron transfer pathways. The experimental rate constants for the dehalogenase are from refs 2b and 2i, and the standard potential is from ref 2f. Data point for B12, see Supporting Information. Blue triangle and square: anion radicals of DMNB and TPN, respectively.

the value found for D_{CF} upon fitting the experimental data is too large as compared to that of other compounds, such as polychloroalkanes, for which the value of D_{CF} is experimentally known.[7] In the transposition of the electrochemical data to homogeneous reactions involving an outersphere electron donor, we may therefore take these values of D_{CF} as upper limits. Since the reorganization energy is a decreasing function of D_{CF}, homogeneous rate constants predicted in this way for the concerted pathway are therefore upper limits.

The homogeneous self-exchange solvent reorganization energies may be derived from[9]

$$\lambda_{0,\text{self-exchange}}^{\text{hom}}(\text{eV}) = 1.75/a\ (\text{Å}) \tag{5}$$

All the reactants, PCE, TCE, Co(I)corrin, aromatic hydrocarbons, have approximately the same radius corresponding to $\lambda_{0,\text{self-exchange}}^{\text{hom}} \cong 0.5$ eV. Thus, in the stepwise case, the reorganization total energy corresponding to the reaction of any outersphere reactants of that size with PCE and TCE is given by

$$\lambda_{\text{step}}^{\text{hom}}(\text{eV}) = (0.5 + 0.5)/2 + \lambda_i(\text{eV}) \tag{6}$$

In the concerted case, the self-exchange solvent reorganization energy for the RCl/R$^\bullet$ + Cl$^-$ couple varies between a value corresponding to the PCE (or TCE) radius, 0.5 eV, to a value corresponding to the Cl$^-$ radius, 0.967 eV, as results from the application of eq 5. Weighting the two limiting values with the factors $(1 - \alpha)$ and α, respectively, one obtains

$$\lambda_{0,\text{conc}}^{\text{hom}}(\text{eV}) = [0.5 + 0.5(1 - \alpha) + 0.967\alpha]/2 \tag{7}$$

The total reorganization energy is thus derived from eqs 4 and 7.

In each case, λ and ΔG° may thus be obtained for any value of the outersphere electron donor standard potential.[10] The activation/driving force plots for each pathway can then be derived from eq 1 and from $k = Z \exp(-\Delta G^{\ddagger}/RT)$, where the pre-exponential factor, Z, is taken as equal to 3×10^{11} M^{-1} s^{-1} on average.[9]

The passage between the stepwise and concerted pathway observed upon decreasing the driving force (from the blue to the red curve in Figure 2) is a well-documented question, theoretically and experimentally. The decrease of the driving force is represented by the cyan arrow in Figure 1.[11]

In view of the number of approximations embodied in the above analysis, it is interesting to see if the reaction with outersphere electron donors, such as aromatic anion radicals, matches the predictions represented in Figure 2. That this is indeed the case is shown in Figure 2, where the blue points represent the reaction of PCE with the anion radicals of dimethylnitrobenzene (DMNB) and terephthalonitrile (TPN). The rate constants were derived from cyclic voltammetric redox catalysis experiments (see Supporting Information).[12]

It clearly appears that the electron transfer mechanism is not consistent with the rate constants that have been measured for the reaction of vitamin B12 and of the dehalogenase with PCE. The gaps are of 7 and 12 orders of magnitude, respectively. The same conclusion holds for the reaction of the enzyme with TCE. The actual mechanism, therefore, involves more intimate interactions between the electron donor and the substrate in which the PCE (or TCE) molecule enters the cobalt coordination sphere, such as those listed in the Supporting Information.

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Supporting Information Available: Reagent formulas, derivation of the rate constants by redox catalysis, and possible mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Westrick, J. J.; Mello, J. W.; Thomas, R. F. *J. Am. Water Works Assoc.* **1984**, *76*, 52. (b) Leisinger, T.; Brunner, W. In *Biotechnology*; Rehm, H.-J., Reed, G., Eds.; VCH Verlagsgesellschaft: Weinheim, Germany, 1986; Vol. 8, pp 475−513. (c) Squillace, P. J.; Moran, M. J.; Lapham, W. W.; Price, C. V.; Clawges, R. M.; Zogorski, J. S. *Environ. Sci. Technol.* **1999**, *33*, 4176. (d) Doherty, R. E. *Environ. Forensics* **2000**, *1*, 69. (e) Squillace, P. J.; Scott, J. C.; Moran, M. J.; Nolan, B. T.; Kolpin, D. W. *Environ. Sci. Technol.* **2002**, *36*, 1923.

(2) (a) Neumann, A.; Wohlfarth, G.; Diekert, G. *Arch. Microbiol.* **1995**, *163*, 276. (b) Neumann, A.; Wohlfarth, G.; Diekert, G. *J. Biol. Chem.* **1996**, *271*, 16515. (c) Magnuson, J. K.; Stern, R. V.; Gossett, J. M.; Zinder, S. H.; Burris, D. R. *Appl. Environ. Microbiol.* **1998**, *64*, 1270. (d) Holliger, C.; Wohlfarth, G.; Diekert, G. *FEMS Microbiol. Rev.* **1999**, *22*, 383. (e) Maillard, J.; Schumacher, W.; Vasquez, F.; Regeard, C.; Hagen, W. R.; Holliger, C. *Appl. Environ. Microbiol.* **2003**, *69*, 4628. (f) Kräutler, B.; Fieber, W.; Ostermann, S.; Mario, F.; Ongan, K.-H.; Gruber, K.; Kratky, C.; Mikl, C.; Siebert, A.; Diekert, G. *Helv. Chim. Acta* **2003**, *86*, 3698. (g) In the enzyme extracted from *dehalospirillum multivorans*, norpseudovitamin B12, rather than vitamin B12, serves as the prosthetic group (see Supporting Information).[2f] (h) Schumacher, W.; Holliger, C.; Zehnder, A. J. B.; Hagen, W. R. *FEBS Lett.* **1997**, *409*, 421. (i) Neumann, A.; Siebert, A.; Trescher, T.; Reinhardt, S.; Wohlfarth, G.; Diekert, G. *Arch. Microbiol.* **2002**, *177*, 420.

(3) (a) Glod, G.; Angst, W.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 253. (b) Shey, J.; van der Donk, W. A. *J. Am. Chem. Soc.* **2000**, *122*, 12403.

(4) Follett, A. D.; McNeill, K. *J. Am. Chem. Soc.* **2005**, *127*, 844.

(5) Savéant, J.-M. Electron Transfer, Bond Breaking and Bond Formation. In *Advances in Physical Organic Chemistry*; Tidwell, T. T., Ed.; Academic Press: New York, 2000; Vol. 35, pp 117−192.

(6) (a) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829. (b) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 11908. (c) Cardinale, A.; Gennaro, A. Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2002**, *124*, 13533.

(7) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 10729.

(8) Energies in electronvolts, potentials in volts.

(9) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

(10) In the concerted case, the determination of λ requires the value of α, which itself depends on λ and ΔG° through eq 2. The problem is solved by applying an iterative procedure, which happens to converge rapidly.

(11) (a) Andrieux, C. P.; Savéant, J.-M. *J. Electroanal. Chem*. **1986**, *205*, 43. (b) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864. (c) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 7158. (d) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1999**, *121*, 7158. (e) Costentin, C.; Hapiot, P.; Médebielle, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 4451.

(12) Nadjo, L.; Savéant, J.-M.; Su K. B. *J. Electroanal. Chem.* **1985**, *196*, 23.

(13) Argüello, J. E.; Costentin, C.; Griveau S.; Savéant, J.-M. *J. Am. Chem. Soc.* **2005**, *127*, 5049.

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