



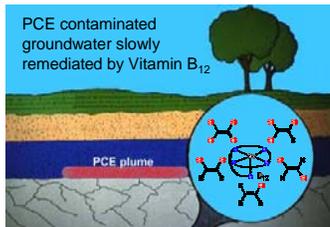
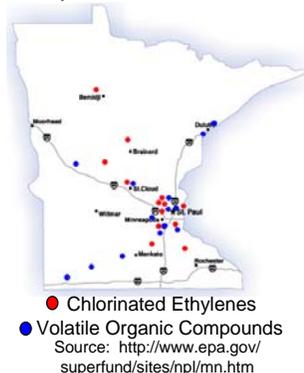
2004 EPA STAR Graduate Fellowship Conference *Next Generation Scientists—Next Opportunities*

Aqueous Reductive Dehalogenation of Chlorinated Ethylenes for Groundwater Remediation

Overview

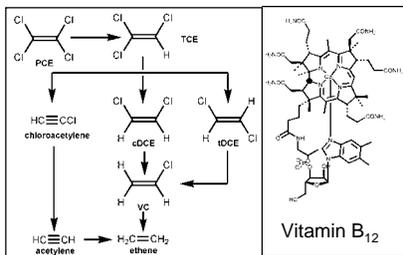
Chlorinated ethylenes (CEs) represent a significant contamination problem for ground and drinking water supplies and are considered priority pollutants by the EPA. Two specific compounds, perchloroethylene (PCE) and trichloroethylene (TCE), are common pollutants because of their heavy use in dry cleaning and as industrial degreasers, respectively. PCE and TCE are carcinogenic and long-lived in the environment but have been found to undergo degradation to lesser chlorinated ethylenes by specific Vitamin B₁₂ containing microbes.¹ Likewise, in the laboratory, CEs can be catalytically dechlorinated with Vitamin B₁₂ in water in the presence of a bulk reductant.^{2,3} In either setting, the products and the rates at which the various compounds are broken down are undesirable. This research began with a search for synthetic catalysts to increase the rate of dechlorination. A water soluble cobalt containing porphyrin (TCPP)Co was identified and found to be at least one order of magnitude faster, against all CE substrates, than B₁₂. The factors controlling degradation rates and product selection for (TCPP)Co have been studied.

Superfund sites in MN



Vitamin B₁₂ degradation of PCE

Vitamin B₁₂ is the dominant natural catalyst for degrading CE pollutants. The main products formed from degradation of either PCE or TCE are the result of sequential removal of chlorine atoms, such that PCE yields TCE, and TCE yields a mixture of *cis* and *trans*-DCE. As the Cl atoms are removed, the pollutant toxicity profiles change from carcinogenic (PCE/TCE) to carcinogenic/acutely toxic (DCE, VC) and finally to benign (acetylene and ethylene).

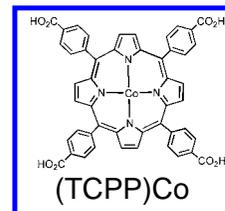


Scientific Approach

We wish to develop catalysts that have higher activity, are less expensive, and whose structures are more easily modified for tuning of chemical and physical properties than their nature-based precursors.

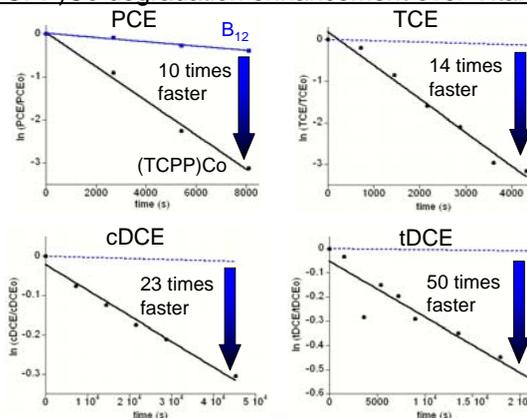
Research Highlights

From approximately 25 initial candidates, one highly-active, dehalogenation catalyst, (TCPP)Co, was identified and studied in depth. While detoxification of PCE follows a similar pathway as B₁₂, (TCPP)Co is between one and two orders of magnitude faster.



This synthetic catalyst has been studied in detail with kinetic and spectroscopic measurements to determine the robustness of its dehalogenation including: dependence on catalyst and bulk reductant concentration, the effect of various inhibitors, viability of catalytic cycle intermediates, as well as the role of pH and temperature on reactivity. (TCPP)Co dehalogenation, while pH sensitive, is quite durable and remains active in the presence of common metal cations or organic inhibitors, which are found in the environment.

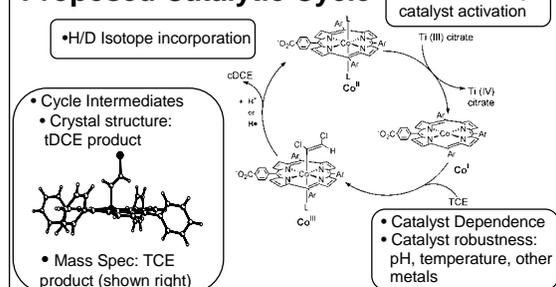
(TCPP)Co degradation enhancement over Vitamin B₁₂



Impact

This work has led to a new, highly-active dechlorination catalyst, (TCPP)Co. It may also yield new catalysts with tunable properties, which will make them more useful for engineered dechlorination systems. In addition, the insights gained regarding the dechlorination mechanism may allow for the selective production of non-toxic, benign dechlorination products.

Proposed Catalytic Cycle



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Selected References

- Gantzer, C. J.; Wackett, L. P., *Environ. Sci. Technol.* **1991**, 25, (4), 715-22.
- Glod, G.; Angst, W.; Holliger, C.; Schwarzenbach, R. P., *Environ. Sci. Technol.* **1997**, 31, (1), 253-260.
- Glod, G.; Brodmann, U.; Angst, W.; Holliger, C.; Schwarzenbach, R. P., *Environ. Sci. Technol.* **1997**, 31, (11), 3154-3160.