

## Photochemical Dehalogenation of DDT Catalyzed by Hydrophobic Vitamin B<sub>12</sub>

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A Co(I) species of vitamin B<sub>12</sub> is a supernucleophile and reacts with an alkyl halide to form an alkylated complex with dehalogenation. The superior ability of vitamin B<sub>12</sub> for reductive dehalogenation prompted us to investigate the catalysis of a vitamin B<sub>12</sub> model complex for degradation of various halogenated organic compounds. We have been dealing with a hydrophobic vitamin B<sub>12</sub>,<sup>1</sup> heptamethyl cobyrinate perchlorate [Cob(II)7C<sub>1</sub>ester]ClO<sub>4</sub>, which has ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B<sub>12</sub>, and performed various enzymic reactions, mainly isomerization reactions leading to the intramolecular exchange of a functional group and a hydrogen atom, using hydrophobic vitamin B<sub>12</sub> derivatives as catalysts.<sup>2</sup> In the course of these studies, hydrophobic vitamin B<sub>12</sub> derivatives were found to act as an excellent model compound for the functional simulation of vitamin B<sub>12</sub> enzyme.<sup>3,4</sup>

Among the reported methods for dehalogenation of chlorinated organic compounds, the electrochemical method has various advantages, such as cleanness and energy efficiency, and is proved to be an excellent approach for degradation of various halogenated organic compounds. Among the chlorinated organic compounds, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (**DDT**) is characterized by a pronounced insecticidal property and has been used worldwide for the last several decades despite its known hazardous effects on human health and wildlife. Because of recent environmental concerns, there is pressing need for efficient methods for degradation of such chlorinated compounds accumulated in the soil. Therefore, much attention will be focused on the reaction between the hydrophobic vitamin B<sub>12</sub> and **DDT** under electrochemical conditions. In this paper, electrolysis of **DDT** catalyzed by hydrophobic vitamin B<sub>12</sub> was carried out as shown in Scheme 1.

The electrolyses were carried out at -1.4 V vs. Ag/AgCl in a cylindrical three-electrode cell which was divided into two internal compartments with a single sheet of microporous polypropylene membrane equipped with a platinum mesh cathode and a zinc plate anode. After the electricity of 1.4 electron/molecule based on the substrate was passed, almost no electrolysis current was detected. Then, the products were analyzed by the procedure described in the experimental section. **DDT** was decomposed over 80% based on its initial concentration, and the turnover number based on the hydrophobic vitamin B<sub>12</sub> as a catalyst was ca.80. The dechlorinated products, **DDD**, **DDE**, **DDMU** and dimers **TTDB** (*E/Z*) were detected by HPLC and GC-MS analysis. Reductive dechlorination of **DDT** did not proceed under the corresponding conditions without hydrophobic vitamin B<sub>12</sub> as a catalyst. In addition, it should be noted that the catalyst was recovered quantitatively after the electrolysis based on electronic and mass spectroscopic analysis.

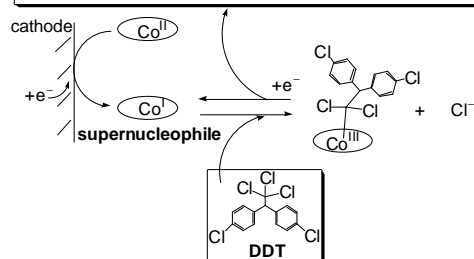
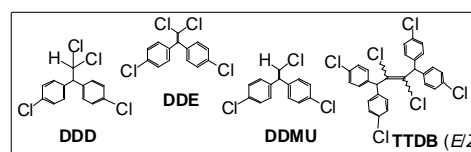
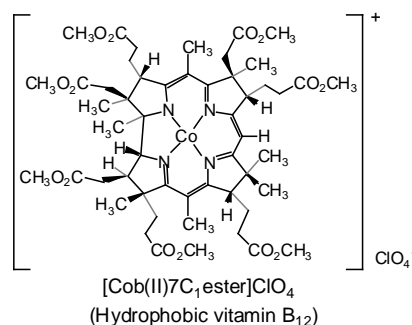
As a next step, we used Ru(II)(bpy)<sub>3</sub> as a photosensitizer as shown in Scheme 2. We tried to

construct hydrophobic vitamin B<sub>12</sub> and Ru(II)(bpy)<sub>3</sub> photo-sensitizer-catalyzed dechlorination system. As **DDT** was irradiated with visible light in the presence of a catalytic amount of [Cob(II)7C<sub>1</sub>ester]ClO<sub>4</sub> and 50 equivalent moles of Ru(II)(bpy)<sub>3</sub> and triethanol amine, dechlorination reaction efficiently proceeded to form **DDD**.

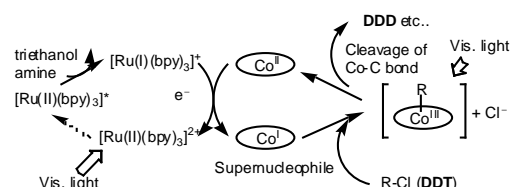
In conclusion, the environmental pollutant **DDT** was dechlorinated *via* formation of the cobalt-carbon bond under electrochemical and photochemical conditions. The hydrophobic vitamin B<sub>12</sub> is one of the best catalysts acting as an electrolysis mediator in the present system.

### References

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- 2 Y. Hisaeda, et al., *Coord. Chem. Rev.*, **198**, 21 (2000).
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Scheme 1.



Scheme 2.