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Photochemical dechlorination of DDT catalyzed by a hydrophobic vitamin B_{12} and a photosensitizer under irradiation with visible light

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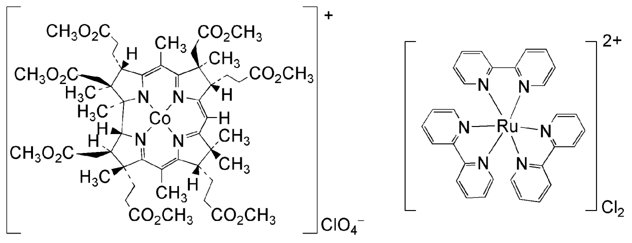
Dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) was catalyzed by a hydrophobic vitamin B_{12}, heptamethyl cobyrinate perchlorate, with a visible light irradiation system containing a $[Ru(II)(bpy)_3]Cl_2$ photosensitizer, and the hydrophobic vitamin B_{12} showed high catalytic efficiency and stability during the reaction.

It is well known that the Co(I) species of cobalamin and related cobalt complexes are supernucleophiles and react with an alkyl halide to form alkylated complexes with dehalogenation.[1–4] We have been working on a hydrophobic vitamin B_{12}, heptamethyl cobyrinate perchlorate $[Cob(II)7C_1ester]ClO_4$, which has ester groups in place of the peripheral amide moieties of the naturally occurring cobalamin as shown in Chart 1,[5] and performed dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (**DDT**) using a hydrophobic vitamin B_{12} as electrochemical mediator in DMF.[6] It is shown in these studies that the hydrophobic vitamin B_{12} is clearly a promising catalyst for dehalogenation of chlorinated organic compounds. Because of recent environmental concerns, there is a pressing need for efficient methods for degradation of such chlorinated compounds accumulated in the soil.[7,8] Therefore, much attention will be focused on the reaction between the hydrophobic vitamin B_{12} and **DDT** in various reaction systems. In this paper, dechlorination of **DDT** in a visible light irradiation system catalyzed by hydrophobic vitamin B_{12} was carried out as shown in Scheme 1.

$[Ru(II)(bpy)_3]Cl_2$ has been extensively studied for its facile photoexcitation properties, and the excited species is quenched by sacrificial triethanolamine to form $[Ru(I)(bpy)_3]^+$.† The redox potential of $[Ru(II)(bpy)_3]Cl_2$ for the Ru(II)/Ru(I) couple is −1.35 V *vs.* SCE in CH_3CN.[9,10] And redox potentials for the Co(II)/Co(I) couple of hydrophobic vitamin B_{12} in various organic solvents, such as DMF, DMSO, CH_3CN and MeOH were observed at −0.61 – −0.65 V *vs.* SCE.[11] Thus, hydrophobic vitamin B_{12} would be reduced to a Co(I) species by the $[Ru(II)(bpy)_3]Cl_2$ photosensitizer in the presence of sacrificial reductant under irradiation of visible light. Therefore, we tried to construct a hydrophobic vitamin B_{12} and $Ru(II)(bpy)_3$ photosensitizer-catalyzed dechlorination system.‡

As **DDT** was irradiated with visible light in the presence of a catalytic amount of $[Cob(II)7C_1ester]ClO_4$ and 50 mole equivalents of $Ru(II)(bpy)_3$, the dechlorination reaction efficiently proceeded as shown by entry 1 in Table 1. **DDT** was almost decomposed based on its initial concentration to form 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (**DDD**) as major product (reaction (1)). A small amount of 1,1-bis(4-chlorophenyl)-2,2-dichloroethylene (**DDE**) was also formed during the reaction. The turnover number based on the hydrophobic vitamin B_{12} as a catalyst was 77. The dechlorination reaction did not proceed in the dark as shown by entry 3 in Table 1. The reaction also did not proceed under the corresponding conditions without the hydrophobic vitamin B_{12} catalyst or the Ru complex as shown by entries 4 and 5 in Table 1, respectively. It should be noted that the hydrophobic vitamin B_{12} catalyst was recovered quantitatively after the reaction based on electronic and mass spectrometric analysis. In contrast, when an imine/oxime-type complex which is a well-known functional model compound of cobalamin, $[Co(III)\{C_2(DO)(DOH)pn\}Br_2]$, $C_2(DO)(DOH)pn$ is N^2,$N^{2\prime}$-propanediyl-bis(2,3-pentanedione 2-imine 3-oxime),[12] was used as catalyst,§ conversion of **DDT** was only 34% as shown by entry 2 in Table 1. The low catalytic activity was due to the low stability of the complex since the complex was almost totally decomposed during the reaction, which was exhibited by mass spectrometric analysis. Therefore, the hydrophobic vitamin B_{12} is a tough and excellent catalyst in the reaction.



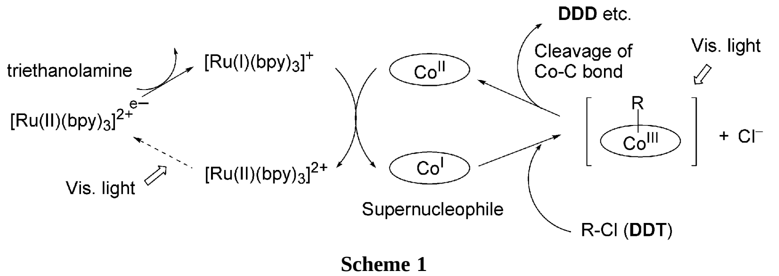
$[Cob(II)7C_1ester]ClO_4$
(Hydrophobic vitamin B_{12})

$[Ru(II) (bpy)_3]Cl_2$

Chart 1

DDT **DDD** (1)

When the reaction was carried out in the presence of CH_3I as a strong electrophile, dechlorination of **DDT** was almost inhibited as shown by entry 6 in Table 1. It is likely that the nucleophilic Co(I) complex is formed as an active species during the reaction. The reaction mechanism was also examined by the spin-trapping technique with α-phenyl *N*-(*tert*-butyl)nitrone (PBN).[13,14] An EPR spectrum was observed for the PBN spin adduct formed during the reaction: g = 2.006, A_N = 15.2 G, A_H = 3.5 G (10^4 G = 1 Tesla).



Scheme 1

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Table 1 Dechlorination of **DDT** catalyzed by cobalt complexes[a]

Entry	Catalyst	Conversion[b] (%)	Product yields[c] DDD	DDE	TN[d]
1	$[\mathrm{Cob(II)7C_1ester}]\mathrm{ClO_4}$[e]	99	71	6	77
2	$[\mathrm{Co(III)\{C_2(DO)(DOH)pn\}Br_2}]$	34	17	2	19
3	$[\mathrm{Cob(II)7C_1ester}]\mathrm{ClO_4}$[f]	Trace	—	—	—
4	None	8	1	Trace	—
5	$[\mathrm{Cob(II)7C_1ester}]\mathrm{ClO_4}$[g]	21	5	2	7
6	$[\mathrm{Cob(II)7C_1ester}]\mathrm{ClO_4}$[h]	1	1	—	1

[a] Dechlorination reactions were carried out under N_2 atmosphere with irradiation of 500 W tungsten lamp for 3 h. Initial concentration: catalyst, 5.0×10^{-4} M; **DDT**, 5.0×10^{-2} M; $[\mathrm{Ru(II)(bpy)_3}]\mathrm{Cl_2}$, 2.5×10^{-2} M; triethanolamine, 5.0×10^{-1} M, solvent: EtOH. [b] Conversion was estimated by the recovery of **DDT**. [c] Products were analyzed by NMR, HPLC and GC-MS. [d] Total turnover number (TN) based on the initial amount of the catalyst. [e] 1,1,4,4-Tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene was also formed as a minor product with 6% (*E*, 5%; *Z*, 1%) yield. [f] The reaction was carried out in the dark. [g] In the absence of $[\mathrm{Ru(II)(bpy)_3}]\mathrm{Cl_2}$. [h] In the presence of $[\mathrm{CH_3I}]$, 5.0×10^{-1} M.

This result indicates that a radical species is generated as the electrolysis intermediate under the present conditions.

A plausible reaction mechanism is proposed as follows. The Co(II) complex is reduced to the Co(I) species by the photosensitizer, and the corresponding alkylated complex is generated by the reaction of the supernucleophilic Co(I) species with **DDT**. The cobalt–carbon bond of the alkylated complex is subsequently cleaved by photolysis to form the substrate radical and Co(II) species. The substrate radical will abstract hydrogen to form **DDD** as the main product. **DDE** may be formed by β-elimination or disproportionation of the substrate radical.

In conclusion, the dechlorination of **DDT** was carried out in EtOH in the presence of a catalytic amount of hydrophobic vitamin B_{12} and a photosensitizer under irradiation with visible light. The present system is superior to chemical reductant systems from the viewpoint of green chemistry, and is a simpler and more facile system than the conventional electrochemical system. The hydrophobic vitamin B_{12} is one of the best catalysts acting in the present system.

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Notes and references

† UV-vis spectrum of $[\mathrm{Ru(II)(bpy)_3}]\mathrm{Cl_2}$ (2.5×10^{-5} M) in ethanol was changed to that of $[\mathrm{Ru(I)(bpy)_3}]^+$ in the presence of triethanolamine (5.0×10^{-4} M) under irradiation of visible light; absorption maxima at 292, 350, 460 and 510 nm.

‡ The dechlorination of **DDT** was carried out in EtOH under N_2 in the presence of $[\mathrm{Cob(II)7C_1ester}]\mathrm{ClO_4}$ with irradiation from a 500 W tungsten lamp. Initial concentrations: cobalt complex, 5.0×10^{-4} M; **DDT**, 5.0×10^{-2} M; $[\mathrm{Ru(II)(bpy)_3}]\mathrm{Cl_2}$, 2.5×10^{-2} M; triethanolamine, 5.0×10^{-1} M. After the reaction, EtOH was removed by evaporation under reduced pressure and 30 mL of $CHCl_3$ were added to the residue. The chloroform layer was washed with water (3 × 40 mL) and dried with Na_2SO_4. And then, the filtrate was concentrated to dryness. The residue was passed through a silica gel short column eluting with $CHCl_3$ to remove hydrophobic vitamin B_{12}, and the products were analyzed by HPLC, NMR and GC-mass spectroscopy.[6]

§ The redox couple of Co(II)/Co(I) for $[\mathrm{Co(III)\{C_2(DO)(DOH)pn\}Br_2}]$ is −0.69 V *vs*. SCE in DMF containing of 0.1 M *n*-$\mathrm{Bu_4NClO_4}$.

1 G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, 1969, **91**, 3341.
2 G. N. Schrauzer, E. Deutsch and R. J. Windgassen, *J. Am. Chem. Soc.*, 1968, **90**, 2441.
3 H. Shimakoshi, A. Nakazato, T. Hayashi, Y. Tachi, Y. Naruta and Y. Hisaeda, *J. Electroanal. Chem.*, 2001, **507**, 170.
4 H. Shimakoshi, M. Tokunaga, K. Kuroiwa, N. Kimizuka and Y. Hisaeda, *Chem. Commun.*, 2004, 50.
5 Y. Murakami, Y. Hisaeda and A. Kajihara, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3642.
6 H. Shimakoshi, M. Tokunaga and Y. Hisaeda, *Dalton Trans.*, 2004, 878.
7 M. M. Häggblom and I. D. Bossert, eds., *Dehalogenation Microbial Processes and Environmental Applications*, Kluwer Academic Publishers, Boston, 2003.
8 H. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2002, **102**, 4009.
9 R. Ziessel, J. Hawecker and J. M. Rehn, *Helv. Chim. Acta*, 1986, **69**, 1065.
10 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. V. Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
11 Y. Murakami, Y. Hisaeda, A. Kajihara and T. Ohno, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 405.
12 P. J. Toscano and L. G. Marzilli, *Prog. Inorg. Chem.*, 1984, **31**, 105.
13 A. J. Bard, J. C. Gilbert and R. D. Goodin, *J. Am. Chem. Soc.*, 1974, **96**, 620.
14 E. E. Bancroft, H. N. Blount and E. G. Janzen, *J. Am. Chem. Soc.*, 1979, **101**, 3692.