Recycled Catalysis of a Hydrophobic Vitamin B_{12} in an Ionic Liquid

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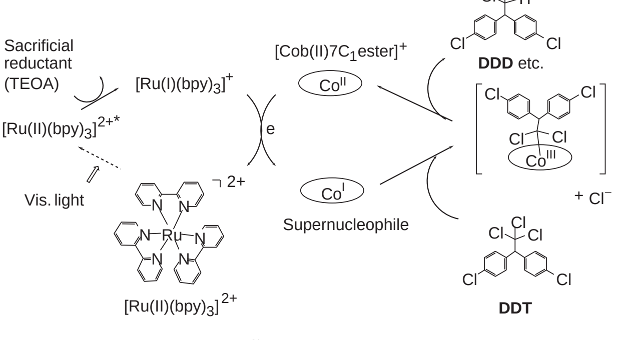
Recycled use of a hydrophobic vitamin B_{12}, heptamethyl cobyrinate perchlorate, in the dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) with a visible light irradiation system containing a $[Ru(II)(bpy)_3]Cl_2$ photosensitizer was achieved using an ionic liquid as reaction medium.

Immobilization of a catalyst onto the surface of inorganic materials such as metal, silica, and glass is a desirable approach for establishment of "Green Chemistry" since the catalyst is easily separated from the reaction medium and reused.[1] Recently, we synthesized a vitamin B_{12} derivative-modified Pt electrode which showed efficient catalysis in electroorganic reaction.[2] As direct modification of a catalyst onto the matrix provided the above advantage, immobilization of the catalyst sometimes required complicated chemical modification of the catalyst. To solve this problem, we report herein a practical recycling procedure of a vitamin B_{12} derivative for catalyst involving the use of an ionic liquid as reaction medium. Ionic liquids have various advantages as a reaction medium because of their low melting point, high polarity, good conductivity, negligible vapor pressure, non-flammability, and good solubility for many organic and inorganic compounds.[3] The ionic liquid [bmim][PF_6] ($[bmim]^+$ = 1-butyl-3-methyl imidazolium cation) is an excellent solvent for 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,[4] but is immiscible with diethyl ether and water that extract reaction products.[3] Therefore, dissolved hydrophobic vitamin B_{12} in an ionic liquid was just as though it was immobilized in ionic liquid, and it is easily separated from products and may be reused for further reaction.

Recently, we reported the dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (**DDT**) using a hydrophobic vitamin B_{12} as catalyst with a visible light irradiation system containing a $[Ru(II)(bpy)_3]Cl_2$ photosensitizer in ethanol as shown in Scheme 1.[5] In the reaction, hydrophobic vitamin B_{12} was presumably reduced to its Co(I) species by electron transfer from the Ru photosensitizer and showed high stability as well as high dechlorination efficiency. Thus in this study, we applied this clean photochemical reaction to an ionic liquid medium system.



Scheme 1.

Before the catalytic reaction, we examined the reductive formation of a Co(I) species of hydrophobic vitamin B_{12} in an ionic liquid by ESR spectroscopy in the presence of a photosensitizer under irradiation with visible light. The ESR signal ascribed to a Co(II) low spin of $[Cob(II)7C_1ester]^+$ [4] disappeared after irradiation with visible light in the presence of $[Ru(II)(bpy)_3]Cl_2$ and sacrificial reductant, triethanolamine (TEOA) as shown in Figure 1.[6]

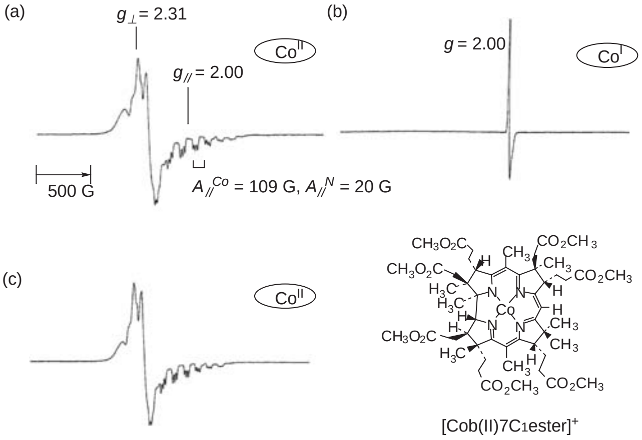
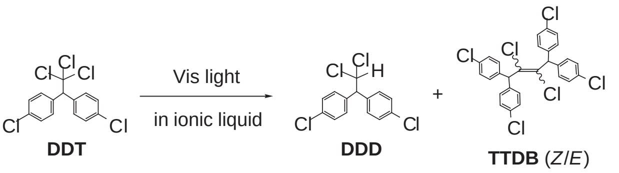


Figure 1. ESR spectra of [Cob(II)7C_1ester]ClO_4 in the presence of $[Ru(II)(bpy)_3]Cl_2$ and triethanolamine (TEOA) in [bmim][PF_6]-CH_3CN (3:7 v/v) at 77 K under anaerobic condition. (a) Before irradiation with visible light, (b) after irradiation with visible light, (c) after air-oxidation of solution (b).

The ESR signal reappeared with almost the same intensity after air-oxidation. This ESR spectral change suggested that the Co(II) species of hydrophobic vitamin B_{12} was reduced to Co(I) species in its oxidation state by photo-induced electron transfer from the Ru complex. Thus we tried to apply catalytic dechlorination of **DDT** using this system.

When **DDT** was irradiated with visible light in the presence of a catalytic amount of [Cob(II)7C_1ester]ClO_4 and 50 equivalent moles of $[Ru(II)(bpy)_3]Cl_2$ and TEOA in [bmim][PF_6]–CH_3CN (3:7 v/v), dechlorination reaction efficiently proceeded as shown by Entry 1 in Table 1.[7] **DDT** was almost decomposed based on its initial concentration to form 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (**DDD**) as a major product and 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene (**TTDB** (*Z*/*E*))[8,9] were also formed as minor products. The dechlorination reaction did not proceed at various controlled reactions as shown by Entries 2–4 in Table 1. A strong electrophile such as CH_3I completely inhibited the reaction as shown by Entry 5 in

Table 1. Dechlorination of **DDT** catalyzed by hydrophobic vitamin B_{12}[a]



Entry	B_{12}	$[Ru^{II}(bpy)_3]^{2+}$	Vis. light	Conversion of **DDT**/%[b]	Yields/%[c]		
					DDD	TTDB (Z)	TTDB (E)
1[d]	○	○	○	99≈	86	6	1
2	○	○	×	≈1	trace	—	—
3[d]	○	×	○	10	9	trace	trace
4[e]	○	○	○	4	1	—	—
5[f]	○	○	○	trace	trace	—	—

[a]Dechlorination reactions were carried out under N_2 atmosphere with irradiation of 500-W tungsten lamp for 3 h. Initial concentration: [Cob(II)-7C_1ester]ClO_4, 5.0×10^{-4} M; **DDT**, 4.0×10^{-2} M; [Ru(II)(bpy)$_3$]Cl_2, 2.5×10^{-2} M; triethanolamine, 5.0×10^{-1} M, solvent: [bmim][PF_6]–CH_3CN (3:7 v/v). [b]Conversion was estimated by the recovery of **DDT**. [c]Products were analyzed by NMR, HPLC, and GC-MS. [d]A small amount of **DDE** (1,1-bis(4-chlorophenyl)-2,2-dichloroethylene) was formed. [e]In the absence of triethanolamine. [f]The reaction was carried out in the presence of [CH_3I], 4.0×10^{-1} M.

Table 1, and which also showed the supernucleophilic Co(I) species is formed as a reactive intermediate. Dehalogenation of another organic halide such as 1,1-bis(4-methoxyphenyl)-2,2,2-trichloroethane (methoxychlore) also efficiently proceeded, and a monodechlorinated product, 1,1-bis(4-methoxyphenyl)-2,2-dichloroethane, was obtained as a major product.

After the reaction, CH_3CN was removed by evaporation and the resulting precipitation[10] was filtered off; then to the obtained filtrate were added Et_2O and H_2O. Three layers, Et_2O, H_2O, and [bmim][PF_6], were clearly separated. Dechlorinated products such as **DDD**, etc. were extracted in Et_2O and hydrophobic vitamin B_{12}, [Cob(II)7C_1ester]$^+$ remained in the ionic liquid, [bmim][PF_6]. The recovery of hydrophobic vitamin B_{12} in an ionic liquid was over 90% based on UV–vis and MS analysis. Therefore, the hydrophobic vitamin B_{12} is a tough and excellent catalyst in the reaction and could be reused for the successive reaction. The result of recycled use of hydrophobic vitamin B_{12} and ionic liquid in the dechlorination reaction is summarized in Table 2.[11] The reaction proceeded with almost the same efficiency in the 4th Run. And hydrophobic vitamin B_{12} was not decomposed even after the 4th Run which was confirmed by MALDI-TOF-MS.

Table 2. Recycled catalysis of hydrophobic vitamin B_{12}[a]

Run	Conversion of **DDT**/%[b]	Yields/%[c]		
		DDD	TTDB (Z)	TTDB (E)
1st	99≈	86	6	1
2nd	99≈	89	6	1
3rd	99≈	93	5	1
4th	99≈	90	4	1

[a]Dechlorination reactions were carried out under N_2 atmosphere with irradiation of 500-W tungsten lamp for 3 h. Initial concentration: [Cob(II)7C_1ester]ClO_4, 5.0×10^{-4} M; **DDT**, 4.0×10^{-2} M; [Ru(II)-(bpy)$_3$]Cl_2, 2.5×10^{-2} M; triethanolamine, 5.0×10^{-1} M, solvent: [bmim][PF_6]–CH_3CN (3:7 v/v). After the 1st Run, the same amount of **DDT**, [Ru(II)(bpy)$_3$]Cl_2 and triethanolamine were added at each Run (2nd–4th). [b]Conversion was estimated by the recovery of **DDT**. [c]Products were analyzed by NMR, HPLC, and GC-MS.

In conclusion, the dechlorination of **DDT** was carried out in an ionic liquid in the presence of a catalytic amount of hydrophobic vitamin B_{12} and a Ru photosensitizer under irradiation of visible light. The recycled use of hydrophobic vitamin B_{12} in an ionic liquid was demonstrated for the first time.

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References and Notes

1 Special issues on recoverable catalysts and reagents can be found in *Chem. Rev.*, **102**, 3215 (2002).
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5 H. Shimakoshi, M. Tokunaga, T. Baba, and Y. Hisaeda, *Chem. Commun.*, **2004**, 1806.
6 The ESR signal observed in Figure 1b is probably ascribed to a cation radical of triethanolamine but was not analysed further.
7 Counter anion of the [Ru(II)(bpy)$_3$]$^+$ is exchanged from the starting Cl^- to PF_6^- and the PF_6 salt is not dissolved in [bmim][PF_6], thus we used CH_3CN as co-solvent. The dechlorination of **DDT** was carried out in [bmim][PF_6]–CH_3CN(3:7 v/v) under a nitrogen atmosphere in the presence of [Cob(II)7C_1ester]ClO_4 with irradiation of a 500-W tungsten lamp. Initial concentrations: cobalt complex, 5.0×10^{-4} M; **DDT**, 4.0×10^{-2} M; [Ru(II)(bpy)$_3$]Cl_2, 2.5×10^{-2} M; TEOA, 5.0×10^{-1} M. After the reaction, CH_3CN was removed by evaporation under reduced pressure and 30 mL of Et_2O and H_2O was added to the residue. The Et_2O layer was washed with water (3 × 30 mL) and dried with Na_2SO_4. And then, the filtrate was evaporated to dryness. The products were analyzed by HPLC, NMR, and GC-mass spectroscopies.
8 H. Shimakoshi, I. Aritome, M. Tokunaga, and Y. Hisaeda, *Acta Crystallgr.*, **E60**, o1470 (2004).
9 Formation of *Z*-form of TTDB was preferred in an ionic liquid. On the other hand, *E*-form of TTDB was preferably obtained in ethanol. See Ref. 5.
10 The precipitate is [Ru(II)(bpy)$_3$](PF_6)$_2$; ^{1}H NMR (acetone-d_6, 500 MHz): δ 7.57 (3H, m, bpy), 8.05 (3H, d, bpy), 8.21 (3H, td, bpy), 8.81 (3H, d, bpy), ^{13}C NMR: δ 125.2, 128.7, 138.8, 152.6, 158.0. MALDI-MS (m/z): $[M - PF_6]^+$, 715.1. IR (KBr, ν/cm^{-1}), 777 (P–F). Anal. Found: C, 41.86; H, 2.90; N, 9.77%; calcd for $C_{30}H_{24}N_6F_{12}P_2Ru_1$: C, 41.92; H, 2.81; N, 9.78%.
11 A small amount of ionic liquid was lost during the extraction process.

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