

Recycled Catalysis of a Hydrophobic Vitamin B₁₂ in an Ionic Liquid

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Recycled use of a hydrophobic vitamin B₁₂, 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]Cl₂ 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 B₁₂ 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 B₁₂ 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][PF₆] ([bmim]⁺ = 1-butyl-3-methyl imidazolium cation) is an excellent solvent for a hydrophobic vitamin B₁₂, heptamethyl cobyrinate perchlorate [Cob(II)7C₁ester]ClO₄, 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 B₁₂ 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 B₁₂ as catalyst with a visible light irradiation system containing a [Ru(II)(bpy)₃]Cl₂ photosensitizer in ethanol as shown in Scheme 1.⁵ In the reaction, hydrophobic vitamin B₁₂ was pre-

sumably 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.

Before the catalytic reaction, we examined the reductive formation of a Co(I) species of hydrophobic vitamin B₁₂ 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)7C₁ester]⁺ disappeared after irradiation with visible light in the presence of [Ru(II)(bpy)₃]Cl₂ and sacrificial reductant, triethanolamine (TEOA) as shown in Figure 1.⁶

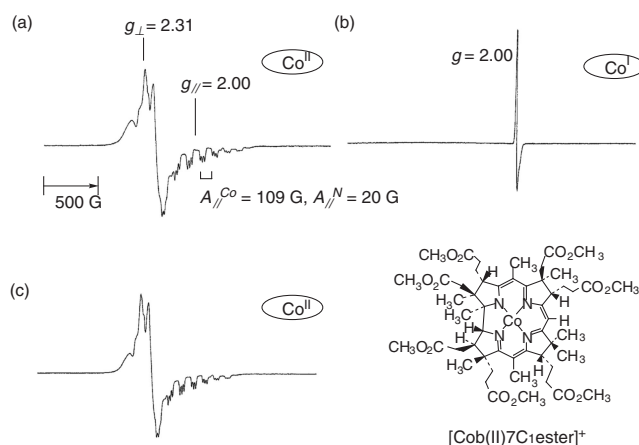
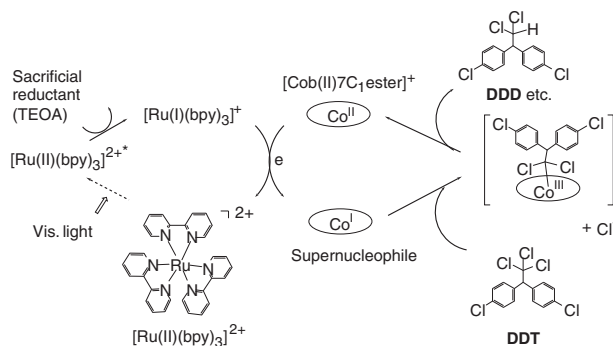


Figure 1. ESR spectra of [Cob(II)7C₁ester]ClO₄ in the presence of [Ru(II)(bpy)₃]Cl₂ and triethanolamine (TEOA) in [bmim][PF₆]-CH₃CN (3:7 v/v) at 77 K under anaerobic condition. (a) Before irradiation with visible light, (b) after irradiation with visible light, (c) after air-oxidation of solution (b).

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 B₁₂ 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)7C₁ester]ClO₄ and 50 equivalent moles of [Ru(II)(bpy)₃]Cl₂ and TEOA in [bmim][PF₆]-CH₃CN (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 CH₃I completely inhibited the reaction as shown by Entry 5 in



Scheme 1.

Table 1. Dechlorination of **DDT** catalyzed by hydrophobic vitamin B₁₂^a

Entry	B ₁₂	[Ru ^{II} (bpy) ₃] ²⁺	Vis. light	Conversion of DDT /%	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	—	—

^aDechlorination reactions were carried out under N₂ atmosphere with irradiation of 500-W tungsten lamp for 3 h. Initial concentration: [Cob(II)-7C₁ester]ClO₄, 5.0 × 10⁻⁴ M; **DDT**, 4.0 × 10⁻² M; [Ru(II)(bpy)₃]Cl₂, 2.5 × 10⁻² M; triethanolamine, 5.0 × 10⁻¹ M, solvent: [bmim][PF₆]-CH₃CN (3:7 v/v). ^bConversion was estimated by the recovery of **DDT**. ^cProducts were analyzed by NMR, HPLC, and GC-MS. ^dA small amount of **DDE** (1,1-bis(4-chlorophenyl)-2,2-dichloroethane) was formed. ^eIn the absence of triethanolamine. ^fThe reaction was carried out in the presence of [CH₃I], 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, CH₃CN was removed by evaporation and the resulting precipitation¹⁰ was filtered off; then to the obtained filtrate were added Et₂O and H₂O. Three layers, Et₂O, H₂O, and [bmim][PF₆], were clearly separated. Dechlorinated products such as **DDD**, etc. were extracted in Et₂O and hydrophobic vitamin B₁₂, [Cob(II)7C₁ester]⁺ remained in the ionic liquid, [bmim][PF₆]. The recovery of hydrophobic vitamin B₁₂ in an ionic liquid was over 90% based on UV-vis and MS analysis. Therefore, the hydrophobic vitamin B₁₂ 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 B₁₂ 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 B₁₂ was

Table 2. Recycled catalysis of hydrophobic vitamin B₁₂^a

Run	Conversion of DDT /%	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

^aDechlorination reactions were carried out under N₂ atmosphere with irradiation of 500-W tungsten lamp for 3 h. Initial concentration: [Cob(II)7C₁ester]ClO₄, 5.0 × 10⁻⁴ M; **DDT**, 4.0 × 10⁻² M; [Ru(II)(bpy)₃]Cl₂, 2.5 × 10⁻² M; triethanolamine, 5.0 × 10⁻¹ M, solvent: [bmim][PF₆]-CH₃CN (3:7 v/v). After the 1st Run, the same amount of **DDT**, [Ru(II)(bpy)₃]Cl₂ and triethanolamine were added at each Run (2nd–4th). ^bConversion was estimated by the recovery of **DDT**. ^cProducts were analyzed by NMR, HPLC, and GC-MS.

not decomposed even after the 4th Run which was confirmed by MALDI-TOF-MS.

In conclusion, the dechlorination of **DDT** was carried out in an ionic liquid in the presence of a catalytic amount of hydrophobic vitamin B₁₂ and a Ru photosensitizer under irradiation of visible light. The recycled use of hydrophobic vitamin B₁₂ in an ionic liquid was demonstrated for the first time.

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References and Notes

- Special issues on recoverable catalysts and reagents can be found in *Chem. Rev.*, **102**, 3215 (2002).
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- The ESR signal observed in Figure 1b is probably ascribed to a cation radical of triethanolamine but was not analysed further.
- Counter anion of the [Ru(II)(bpy)₃]⁺ is exchanged from the starting Cl⁻ to PF₆⁻ and the PF₆⁻ salt is not dissolved in [bmim][PF₆], thus we used CH₃CN as co-solvent. The dechlorination of **DDT** was carried out in [bmim][PF₆]-CH₃CN(3:7 v/v) under a nitrogen atmosphere in the presence of [Cob(II)7C₁ester]ClO₄ 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]Cl₂, 2.5 × 10⁻² M; TEOA, 5.0 × 10⁻¹ M. After the reaction, CH₃CN was removed by evaporation under reduced pressure and 30 mL of Et₂O and H₂O was added to the residue. The Et₂O layer was washed with water (3 × 30 mL) and dried with Na₂SO₄. And then, the filtrate was evaporated to dryness. The products were analyzed by HPLC, NMR, and GC-mass spectroscopies.
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- 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.
- The precipitate is [Ru(II)(bpy)₃](PF₆)₂; ¹H NMR (acetone-d₆, 500 MHz): δ 7.57 (3H, m, bpy), 8.05 (3H, d, bpy), 8.21 (3H, td, bpy), 8.81 (3H, d, bpy), ¹³C NMR: δ 125.2, 128.7, 138.8, 152.6, 158.0. MALDI-MS (*m/z*): [M - PF₆]⁺, 715.1. IR (KBr, *v/cm*⁻¹), 777 (P-F). Anal. Found: C, 41.86; H, 2.90; N, 9.77%; calcd for C₃₀H₂₄N₆F₁₂P₂Ru₁: C, 41.92; H, 2.81; N, 9.78%.
- A small amount of ionic liquid was lost during the extraction process.