Photosensitizing catalysis of the B_{12} complex without an additional photosensitizer

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Photosensitizing catalysis of B$_{12}$ complex without additional photosensitizer

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A cobalamin derivative, heptamethyl cobrinate perchlorate, was activated by UV light irradiation to form a Co(I) species in the presence of triethanolamine and used for a dechlorination reaction, and this photochemical reaction was accelerated in an ionic liquid.

The cobalamin derivative (B$_{12}$) is a cobalt complex with a tetrapyrole ring system (corrin ring) that has emerged in a variety of enzymes such as methylmalonyl CoA mutase, methionine synthase and reductive dehalogenase. Inspired by the unique functions of these enzymes, various catalytic reactions have already been reported using B$_{12}$ model complex such as the 1,2-migration of a functional group, dechlorination of organic chlorides, methylation of heavy metals and thiols, etc. Among the B$_{12}$ model complexes, the corrinoid compound was mostly developed in the B$_{12}$ mimic reaction due to its structure and physicochemical properties similar to natural cobalamin.

Most of the catalytic reactions by the corrinoid compound were achieved using the supernucleophilicity of the reduced form of the Co(I) species. Therefore, all of the catalytic reaction were coupled with a reducing system such as a chemical reductant (NaBH$_4$, Zn, Na amalgam and so on), electrochemical reduction and combined use with a photosensitizer. Recently, we reported the dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) catalyzed by the B$_{12}$ derivative, heptamethyl cobyrinate perchlorate (Co(II) form), with a [Ru(II)(bpy)$_3$]Cl$_2$ photosensitizer by irradiation with visible light. The B$_{12}$ complex was reduced to form the reactive Co(I) species by electron transfer from the ruthenium photosensitizer in the presence of a sacrificial reductant. Although the B$_{12}$ complex showed a high catalytic efficiency in the reaction, a photosensitizer was required for the reaction. If the B$_{12}$ complex itself shows dual properties, photosensitization and catalysis, the catalytic reaction was achieved without any additional photosensitizer. To alleviate this problem, we started to explore the photosensitizing property of the cobalamin derivative and determined the unique photosensitizing property of the B$_{12}$ complex, especially in an ionic liquid. The ionic liquid is a unique ion pair solvent having various properties such as high polarity, good conductivity and negligible vapor pressure. In this paper, the unique photosensitizing property of the B$_{12}$ complex in the ionic liquid and its application for DDT degradation without any photosensitizer are reported (Figure 1).

The heptamethyl cobyrinate perchlorate was first synthesized by Eschenmoser’s group and used by many groups. It shows a high solubility toward not only a variety of organic solvents, but also ionic liquids such as N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([P13][TFSA]) and 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide ([bmim][TFSA]) (Chart 1).

When heptamethyl cobyrinate perchlorate was dissolved in an ionic liquid ([P13][TFSA]) or methanol containing 0.1 M triethanolamine (TEOA) and subsequently irradiated by UV light ($\lambda_{\text{max}} = 365$ nm) under anaerobic conditions, the color of the solution changed from brown to dark green. This photoreaction was well monitored by UV-vis spectroscopy. The UV-vis spectrum of the starting Co(II) form of the B$_{12}$ complex having absorption maxima at 314 nm and 468 nm was changed to a new
spectrum with absorption maxima at 390 and 560 nm which is
typical for the Co(I) state of the B12 complex by UV light
irradiation as shown in Figures 2a (in [P13][TFSA]) and 2b (in
MeOH).

From these UV-vis spectral changes, the rate constant for the
Co(I) formation was determined to be \( k = 2 \times 10^{-4}\ s^{-1}\) and \( 3 \times 10^{-5}\ s^{-1}\) in [P13][TFSA] and MeOH, respectively (ESI†). This
photochemical reaction was ca. 7 times enhanced in the ionic
liquid. In [bmm][TFSA], the B12 complex showed a poor UV-
vis change (Figure S1). Because the imidazolium-type ionic
liquid has a relatively acidic C-H bond at the imidazole ring,9 it
should quench the Co(I) species of the B12 complex.10

The photoreduction of the B12 complex was also investigated
by ESR spectroscopy. The heptamethyl cobrinate perchlorate
showed the typical Co(II) low-spin signal (\( g_1 = 2.51, g_2 = 2.25, g_3 = 2.00, A^{Co} = 63\ G, A^{Co} = 134\ G\) in [P13][TFSA] containing 0.1
M TEOA as shown in Figure 3a.11 After UV light irradiation,
this signal almost disappeared to form the diamagnetic Co(I)
species (Figure 3b). This ESR spectral change also indicated that
the B12 complex was reduced to the Co(I) form by the UV light
irradiation.

Two plausible mechanisms are shown in Figure 4. Once the
Co(II) form of the B12 complex is excited, a ligand (corrin ring)
to the metal charge transfer state may be formed. While the
oxidation state of B12 was Co(III), an ultrafast electronic
relaxation of the excited state vitamin B12 (cyanocobalamin) in
the gas phase was reported by Shafizadeh et al.12 The decay is
interpreted as resulting from a ring to metal charge transfer. A
similar excited state is predicted in the present case, and such a
charge-separated (CS) state (Co(I) cation radical) could be
stabilized in an ion-pair solvent, ionic liquid having a high
polarity, and subsequent electron transfer from TEOA to form the
reduced form of the B12 Co(I) state (Figure 4a). Another
possibility is forming an encounter complex between the excited
B12 complex and TEOA. In this model, electron transfer from
TEOA to the B12 complex in the encounter complex should form
the CS state (Co(I)-TEOA⁺). This charge-separated state could
be stabilized in a polar ionic liquid to prevent a back-electron
transfer process (Figure 4b). To further understand the
photosensitizing property of the B12 complex, ultrafast transition
spectroscopy for the Co(II) state of corrinoid compound is needed.

The catalytic reaction was carried out using DDT as a
substrate. The results are shown in Table 1. After a 2 hr UV
light irradiation, DDT was converted to a monodechlorinated
compound, 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD) in
72 % yield (Entry 1 in Table 1). The reaction did not proceed in
remained in the ionic liquid and was quantitatively recovered as species. This photosensitizing property of the B12 complex was efficiency in the second and third runs (yields of DDD, 2nd 70 % and 3rd 68 %).

After the photoreaction with workup, most of the B12 catalyst remained in the ionic liquid and was quantitatively recovered as confirmed by UV-vis spectra (Figure S2). Therefore, the B12 complex could be reused for the successive reaction. In fact, the DDT dechlorination reaction proceeded with almost the same efficiency in the second and third runs (yields of DDD, 2nd 70 % and 3rd 68 %).

Table 1 Photocatalytic dechlorination of DDT catalyzed by B12 complex.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Irradiation</th>
<th>Yields (%)b</th>
<th>TONc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[P13][TFSA]</td>
<td>UV</td>
<td>72</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>[P13][TFSA]</td>
<td>dark</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>MeOH</td>
<td>UV</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

a Condition: [B12] = 4.4x10^-5 M, [DDT] = 2.2x10^-3 M, [triethanolamine] = 0.1 M. λmax = 365 nm under degassed condition at room temperature. Reaction time: 2 hr.
b Yields were based on initial concentration of the substrate.
c Turnover numbers (TON) were based on [B12].

In summary, the photosensitizing property of the B12 complex under anaerobic conditions was investigated. The reductive quenching of the excited state of the B12 complex by a sacrificial reductant provided the reduced form of the B12 complex, Co(I) species. This photosensitizing property of the B12 complex was used for dechlorination of the pollutant, DDT. Therefore, the results reported here will open a door to the new use of the corrinoid compound in photocatalytic chemistry.

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Notes and references

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1 Electronic supplementary information (ESI) available: Details of experimental procedures. See: DOI: http://dx.doi.org/10.1039/b103999h

2 Black light (UVP, XX-15BLB) was used for the UV light irradiation (1.76 mW cm⁻² at 12-cm distance).

3 The photochemical reaction did not proceed under visible irradiation using a 200-W tungsten lamp with a 420-nm cut-off filter (Sigma Koki, Φ2L) and a heat cut-off filter (Sigma Koki, 30H).

4 In MeOH, the photochemical reaction slowly proceeded without TEOA.

5 MeOH also acts as a weak sacrificial reductant.

6 ‡ This alkylated complex homolysis by UV light is shown in Figure 1.4,13

7 † Quenching of the excited state of the B12 complex by a sacrificial reductant was investigated.

8 After the photoreaction with workup, most of the B12 catalyst remained in the ionic liquid and was quantitatively recovered as species. This photosensitizing property of the B12 complex was efficiency in the second and third runs (yields of DDD, 2nd 70 % and 3rd 68 %).

9 † Quenching of the excited state of the B12 complex by a sacrificial reductant was investigated.

10 The results reported here will open a door to the new use of the corrinoid compound in photocatalytic chemistry.


16 (a) L. Werthemann, R. Keesee and A. Eschenmoser, unpublished results. (b) see L. Werthemann, Dissertation, ETH Zürich (No. 4097), Juris Druck and Velag, Zürich, 1968.


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Photosensitization

UV

Sacrificial reductant

Co$^{II}$

$e^-$

Cl\_Cl\_Cl

Co$^I$

DDT

Catalysis

\[
\begin{align*}
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\end{align*}
\]

+ Cl$^-$

Dechlorination

\[
\begin{align*}
\text{Cl} & \text{H} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\end{align*}
\]

DDD