Hybrid Catalysts

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Oxygen-Controlled Catalysis by Vitamin B_{12}-TiO_2: Formation of Esters and Amides from Trichlorinated Organic Compounds by Photoirradiation

Hisashi Shimakoshi and Yoshio Hisaeda**

Abstract: *An oxygen switch in catalysis of the cobalamin derivative (B_{12})-TiO_2 hybrid catalyst for the dechlorination of trichlorinated organic compounds has been developed. The covalently bound B_{12} on the TiO_2 surface transformed trichlorinated organic compounds into an ester and amide by UV light irradiation under mild conditions (in air at room temperature), while dichlorostilbenes (E and Z forms) were formed in nitrogen from benzotrichloride. A benzoyl chloride was formed as an intermediate of the ester and amide, which was detected by GC-MS. The substrate scope of the synthetic strategy is demonstrated with a range of various trichlorinated organic compounds. A photo-duet reaction utilizing the hole and conduction band electron of TiO_2 in B_{12}-TiO_2 for the amide formation was also developed.*

Organic–inorganic hybrid materials provide various advantages for the design and preparation of heterogeneous catalysts that have been developed for separation and recycling in catalytic chemistry.[1,2] Hybrid materials also show a synergistic effect on catalysis, which has never been achieved by a single catalyst. For example, a metal complex combined with a semiconductor achieves light-driven molecular transformations, such as water splitting,[3] CO_2 reduction,[4] and pollutants decomposition.[5] A band gap excitation in the semiconductor that occurs by light irradiation initiates the reduction and oxidation of reactants at the surface of the semiconductor. The light-driven electron transfer chemistry is a key-step for the reaction. Among semiconductors, titania (titanium dioxide, TiO_2) is widely used in hybrid catalysts because of its abundance, high stability, moderate band gap energy, and usable reduction and oxidation abilities generated by UV light irradiation.[6]

Recently, we synthesized a cobalamin derivative (B_{12}), cobyrinic acid, immobilized on TiO_2 hybrid catalyst where B_{12} was coordinated to the TiO_2 surface by carboxylic groups.[7] As naturally-occurring B_{12}-dependent enzymes catalyze various molecular transformations,[8] this hybrid catalyst mediates various molecular transformations with the B_{12} function by UV light irradiation such as the dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT),[7b] 1,2-migration of a functional group,[7c] H_2 production,[7a] and alkene reduction.[7a] All of these reactions were mediated by the supernucleophilic Co^I form of B_{12} formed by electron transfer from TiO_2 during light irradiation. In general, this type of reaction should be carried out under anaerobic conditions to avoid auto-oxidation of the Co^I species. Furthermore, active oxygen species are generated by the TiO_2, which accelerates the decomposition of the modified compound on the TiO_2.[6]

We now report the development of the distinct oxygen-controlled catalysis by B_{12}-TiO_2 as shown in Figure 1. Trichlorinated organic compounds were transformed into different products depending on whether the reaction was carried out under N_2 or air (oxygen). Recently, Rueping et al. reported an oxygen switch during visible-light photoredox catalysis, and oxygen triggers one of two different pathways to obtain two different types of products from the same starting materials.[9] The progress of visible-light photoredox catalysts has contributed to a wide range of organic synthesis procedures.[10] In our system using a heterogeneous TiO_2 catalyst, valuable esters and amides were obtained from trichlorinated organic compounds under mild conditions (in air at room temperature) by a simple light irradiation and work-up procedure.

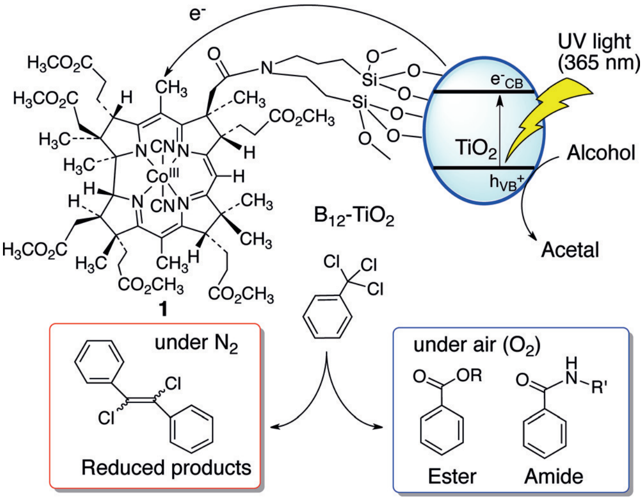

Figure 1. Oxygen-controlled dechlorination of benzotrichloride by B_{12}-TiO_2.

To carry out the aerobic reaction, we newly synthesized a B_{12} derivative having two trimethoxysilyl groups and a Co^{III} metal center, $(CN)_2Cob^{III}6C_1esterCON\{(CH_2)_3Si(OMe)_3\}_2$ (**1**)

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[*] Prof. Dr. H. Shimakoshi, Prof. Dr. Y. Hisaeda
Department of Chemistry and Biochemistry
Graduate School of Engineering, Kyushu University
Fukuoka, 819-0395 (Japan)
E-mail: shimakoshi@mail.cstm.kyushu-u.ac.jp
yhisatcm@mail.cstm.kyushu-u.ac.jp

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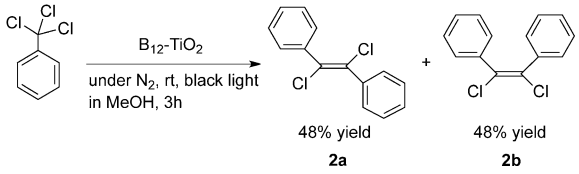
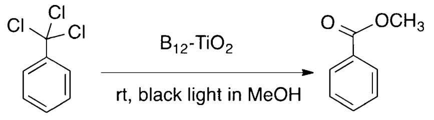
(see the Supporting information), which could be covalently immobilized on the TiO_2 surface (Figure 1). This B_{12} complex is easily and stably bound to the TiO_2 by mixing with TiO_2 (anatase, average surface area: 52 $m^2 g^{-1}$) in MeOH at room temperature. The content of the B_{12} complex on the surface of TiO_2 was 1.37×10^{-5} $mol\,g^{-1}$, and the apparent surface coverage by the B_{12} complex was 2.68×10^{-11} $mol\,cm^{-2}$. This covalently bound B_{12}-TiO_2 hybrid catalyst was characterized by diffuse reflectance (DR) UV/Vis and IR spectroscopies, and TEM (Supporting Information, Figures S5–S7). No mass peak ascribed to B_{12} was detected by MALDI-TOF MS owing to its strong binding on the surface of the TiO_2, which cannot be desorbed by laser irradiation of the MALDI MS analysis (Figure S8). In contrast, B_{12} coordinated to TiO_2 by carboxylic groups was desorbed by laser irradiation of the MALDI MS analysis, and was detected by its corresponding mass peak (Figure S9). Therefore, the covalently bound B_{12}-TiO_2 was more tightly immobilized on TiO_2 and was a suitable catalyst to perform the aerobic photoreaction. In fact, the covalently bound Co^{III} form of B_{12} on the TiO_2 surface was reduced to Co^{I} from Co^{II} by UV light irradiation with absorption maxima at 390 nm and 470 nm, respectively (Figure S10), which was similar to a previous B_{12} (cobyrinic acid)-TiO_2 system.[7] Thus, the Co^{I} form of B_{12} should reacts with various organic halides owing to its supernucleophilicity.[11]

As for catalytic reactions, we first examined the anaerobic dechlorination of benzotrichloride by B_{12}-TiO_2 in MeOH (Supporting information). MeOH was used as a solvent and a hole (h_{VB}^+) consumer of the TiO_2 valence band. 1,2-Dichlorostilbenes (**2a** and **2b**) were quantitatively formed by UV light irradiation under N_2 (each 48%; Scheme 1). The suspended B_{12}-TiO_2 catalyst was easily separated by filtration after the reaction. The content of the B_{12} complex on the surface of TiO_2 was 1.30×10^{-5} $mol\,g^{-1}$ after the reaction, and ca. 95% of B_{12} survived during anaerobic reaction. In this way, the covalently bound B_{12}-TiO_2 hybrid catalyst also works in the dechlorination of organic halides.



Scheme 1. Anaerobic dechlorination of benzotrichloride by B_{12}-TiO_2.

Table 1: Oxidative dechlorination of benzotrichloride to methyl benzoate by B_{12}-TiO_2 or other TiO_2s.[a]



3a

Entry	Catalyst	Time [h]	Atmosphere	Yield [%][b]
1	B_{12}-TiO_2	3	air	99
2	B_{12}-TiO_2	5	O_2	91
3	B_{12}-TiO_2[c]	3	air	0[d]
4	B_{12}-TiO_2[e]	3	air	trace[d]
5	TiO_2	3	air	3
6	Pt-TiO_2[f]	3	air	10
7	B_{12}-TiO_2[g]	3	air	45

[a] [B_{12}-TiO_2] = 10 mg (B_{12}, 2.28×10^{-5} M), [substrate] = 3.0 mM, solvent MeOH 6 mL at room temperature by UV light irradiation (black light, λ_{max} = 365 nm, 1.5 mWcm^{-2} at 10 cm distance). [b] Yield was based on initial concentration of substrate. [c] Dark condition. [d] Most of substrate was recovered. [e] Solvent CH_3CN 6 mL was used instead of MeOH. [f] Pt-TiO_2 = 10 mg (0.15 wt% Pt). [g] B_{12}(cobyrinic acid)-TiO_2 = 8.7 mg (B_{12}, 2.28×10^{-5} M).

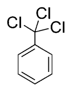
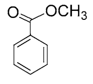
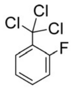
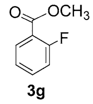
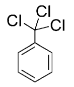
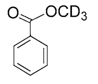
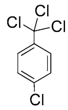
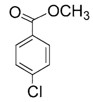
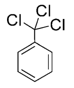
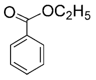
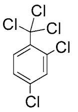
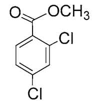
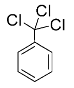
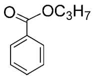
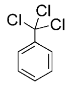
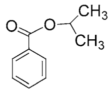
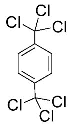
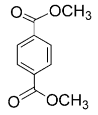
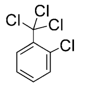
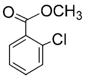
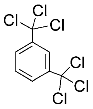
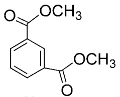
When the reaction was carried out under aerobic conditions (Supporting Information),[12] the product was dramatically changed and all of the chlorines were removed from the substrate. Methyl benzoate was formed in 99% yield (Table 1, entry 1).[13] The reaction also proceeded under oxygen, with the yield of ester decreasing to 91% and requiring 5 h to consume all substrate (Table 1, entry 2). These results suggest that too much oxygen disturbs the reaction, and the reaction proceeds efficiently under atmospheric conditions. Without light irradiation or MeOH (h_{VB}^+ consumer), the reaction did not proceed (Table 1, entries 3 and 4). The B_{12} was also essential for the reaction (Table 1, entries 5 and 6), and the involvement of reactive oxygen species formed directly by TiO_2 in the reaction is considered negligible.[14,15] The previous B_{12}(cobyrinic acid)-TiO_2 also worked (Table 1, entry 7), but the yield of ester was 45% and the catalyst was bleached after the reaction owing to the weak binding of B_{12} on TiO_2.

The reaction was also applied to various benzotrichloride derivatives (Table 2). The esters were obtained in good to high yields (75–99%). When the reactions were carried out in ethanol or *n*-propanol, ethyl benzoate or *n*-propyl benzoate were obtained, respectively. In contrast, in *iso*-propanol, only a 10% yield of *iso*-propyl benzoate was obtained. These results implied that the solvent alcohol works as a h_{VB}^+ quencher of TiO_2, and the quenching efficiency is correlated with the B_{12}-TiO_2 catalytic efficiency.[16] In fact, the oxidized product, dimethyl acetal, was obtained in moderate yield as the reaction proceeded.[17]

When the reaction was applied to other trichlorinated compounds, such as DDT, the yield of the ester (**4a**) was 56% in EtOH, but with a high selectivity (Scheme 2).[18] From 1,1,1-trichloroethane and chloroform, ethyl acetate (**4b**) and ethyl formate (**4c**) were obtained in moderate yields, respectively.[18] As for dihalo benzylic compounds, dichloromethyl benzene showed low reactivity for the reaction,[19] while dibromomethyl benzene afforded moderate yield of the ester (**3a**).[20]

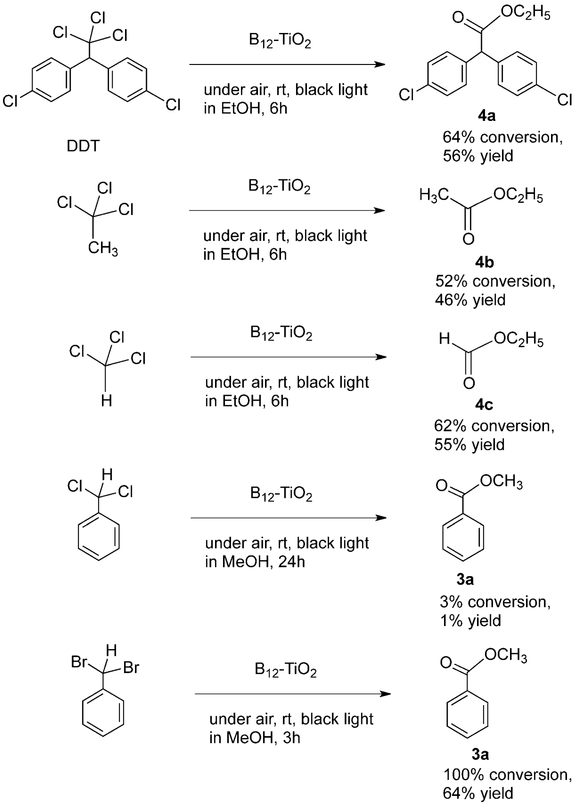
The proposed reaction mechanism is shown in Scheme 3. From the reaction of the Co^{I} species in B_{12}-TiO_2, the dichloromethylbenzene radical (**5**) could be formed from the trichloromethylbenzene. Owing to the electron-withdrawing property of the two chlorine atoms, further reduction by TiO_2 formed the carbanion intermediate (**6**) under anaerobic conditions. The carbanion **6** may lead to a carbene with elimination of the chloride ion. The electrophilic carbene may react with the carbanion **6** to form 1,2-dichlorostilbene (**2a**, **2b**). Though coupling of the radical **5** may produce

Table 2: Oxidative dechlorination of benzotrichloride derivatives by B_{12}-TiO_2 under air.[a]

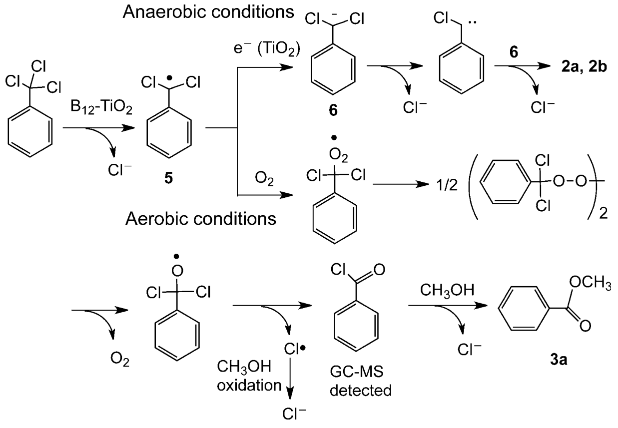
Substrate	Product	Yield [%]	Substrate	Product	Yield [%]
	 **3a**	99		 **3g**	87
	 **3b**	99[b]		 **3h**	93
	 **3c**	92[c]		 **3i**	96
	 **3d**	90[d]			
	 **3e**	10[e]		 **3j**	99[f]
	 **3f**	75		 **3k**	99[f]

[a] $[B_{12}\text{-}TiO_2] = 10$ mg (B_{12}, 2.28×10^{-5} M), [substrate] = 3.0 mM, solvent MeOH 6 mL at room temperature by 3 h UV light irradiation (black light, $\lambda_{max} = 365$ nm, 1.5 mW cm^{-2} at 10 cm distance). [b] Solvent = CD_3OH. [c] Solvent = EtOH. [d] Solvent = *n*-PrOH. [e] Solvent = *i*PrOH. [f] [substrate] = 1.5 mM, 6 h UV light irradiation.

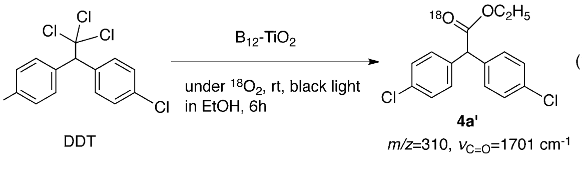
1,1,2,2-tetrachloro-1,2-diphenylethane[21] and, following dechlorination, form 1,2-dichlorostilbenes (**2a** and **2b**),[22] we could not detect such coupling tetrachloro compounds by GC-MS during the reaction. Thus we have excluded it from the proposed mechanism. While under aerobic conditions, the radical **5** may rapidly react with oxygen to form the peroxy radical.[23] The coupling and subsequent elimination of oxygen and disproportionation should form benzoyl chloride as an intermediate.[24] The benzoyl chloride could react with the alcohol solvent to form the ester. In fact, formation of the benzoyl chloride was confirmed by GC-MS during the photoreaction in CH_3CN in which the benzoyl chloride more stably existed than in the alcohol solvent system (Figure S12). Oxygen incorporation into the ester product was also confirmed by using $^{18}O_2$ [Eq. (1)]. In the IR analysis of the ester **4a′**, the ν(ester C=O) peak was shifted to 1701 cm^{-1} from 1733 cm^{-1} of the authentic ester **4a** (^{16}O; Figure S13). In the MS analysis, the parent peak was observed at $m/z = 310$ for **4a′**, while the parent peak for **4a** (^{16}O) was observed at $m/z = 308$ (Figure S14). Therefore, it is clear that one ^{18}O atom was incorporated into the ester as a carbonyl oxygen.[25]



Scheme 2. Scope of the substrate variation.

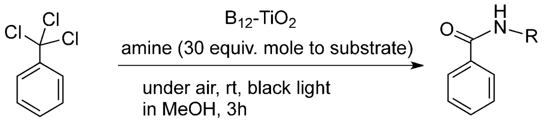


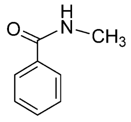
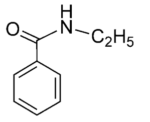
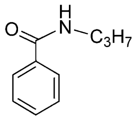
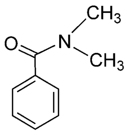
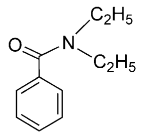
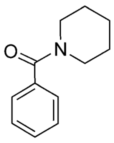
Scheme 3. Proposed reaction mechanism by B_{12}-TiO_2 for dechlorination of benzotrichloride.

 (1)

Detection of the benzoyl chloride under the aerobic conditions prompted us to develop further applications of the B_{12}-TiO_2 catalysis. When the reactions were carried out in the presence of amines (30 equiv mole toward substrate; see the Supporting Information for further details), the corresponding amides (**7a**–**7f**) were efficiently produced in place of the ester (Table 3). As the amine is more reactive to benzoyl

Table 3: B_{12}-TiO_2 catalyzed amidation of benzotrichloride under air.[a]



 **7a** 90% yield	 **7b** 92% yield	 **7c** 95% yield
 **7d** 90% yield	 **7e** 94% yield	 **7f** 79% yield

[a] [B_{12}-TiO_2] = 10 mg (B_{12}, 2.28×10^{-5} M), [benzotrichloride] = 3.0 mM, [amine] = 90 mM, solvent = MeOH 6 mL under air at room temperature by UV light irradiation (black light, λ_{max} = 365 nm, 1.5 mW cm^{-2} at 10 cm distance).

chloride than the alcohol, the corresponding amides were preferentially formed in good to high yields.[28]

During the course of this study, we also established a photo-duet reaction (Figure 2; see the Supporting Information for further details). Both the reduction and oxidation by the conduction band electron (e_{CB}^-) and h_{VB}^+ were directly involved in the product formation. The triethyl amine (TEA) quenches h_{VB}^+ to form the radical cation ($TEA^{\bullet+}$). The sequence reaction of $TEA^{\bullet+}$ could produce diethylamine,[29] which then reacts with benzoyl chloride to form the amide (**7e**),[30] which is a skeleton of chemical insect repellent, *N*,*N*-diethyl-3-methylbenzamide (DEET).[31]

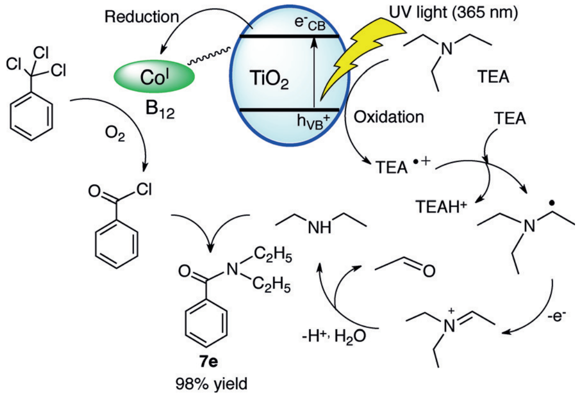


Figure 2. Photo-duet reaction catalyzed by B_{12}-TiO_2.

In summary, we have developed for the first time an aerobic molecular transformation by combining B_{12} with TiO_2. The oxygen-controlled catalysis of the B_{12}-TiO_2 hybrid catalyst dramatically changed the product distribution from a partially dechlorinated compound to an ester or amine. The reactions reported here occurred under mild conditions, that is, room temperature and in air, without a precious reagent, and the catalyst was easy to separate from the products. Ongoing work in our laboratory is focused on the application of this synthetic strategy to other organic syntheses, and also establishing a visible light responsive catalytic system using various visible light responsive TiO_2.[32]

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Keywords: cobalamins · heterogeneous catalysis · oxygen · photocatalysis · titanium dioxide

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[18] Owing to the low reactivity of substrates, a double amount of the catalyst was used (20 mg) and the reaction time was extended to 6 h.

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