

# Oxygen-Controlled Catalysis by Vitamin B<sub>12</sub>-TiO<sub>2</sub>: Formation of Esters and Amides from Trichlorinated Organic Compounds by Photoirradiation

Hisashi Shimakoshi\* and Yoshio Hisaeda\*

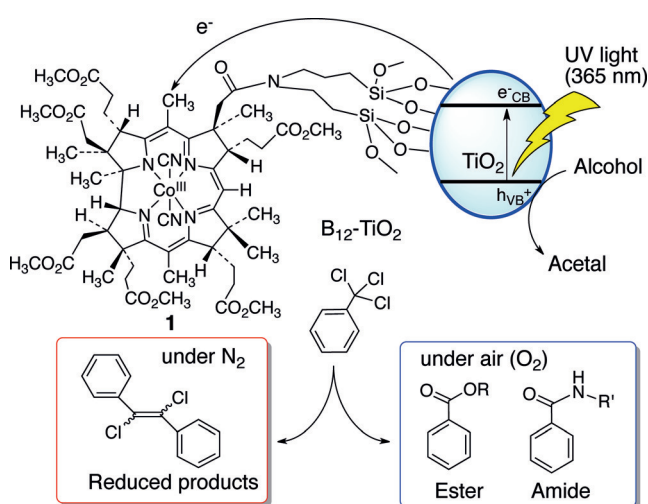
**Abstract:** An oxygen switch in catalysis of the cobalamin derivative (B<sub>12</sub>)-TiO<sub>2</sub> hybrid catalyst for the dechlorination of trichlorinated organic compounds has been developed. The covalently bound B<sub>12</sub> on the TiO<sub>2</sub> surface transformed trichlorinated organic 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<sub>2</sub> in B<sub>12</sub>-TiO<sub>2</sub> 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.<sup>[1,2]</sup> 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,<sup>[3]</sup> CO<sub>2</sub> reduction,<sup>[4]</sup> and pollutants decomposition.<sup>[5]</sup> 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<sub>2</sub>) 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.<sup>[6]</sup>

Recently, we synthesized a cobalamin derivative (B<sub>12</sub>), cobyrinic acid, immobilized on TiO<sub>2</sub> hybrid catalyst where B<sub>12</sub> was coordinated to the TiO<sub>2</sub> surface by carboxylic groups.<sup>[7]</sup> As naturally-occurring B<sub>12</sub>-dependent enzymes catalyze various molecular transformations,<sup>[8]</sup> this hybrid catalyst mediates various molecular transformations with the B<sub>12</sub> function by UV light irradiation such as the dechlorination of 1,1-bis(4-

chlorophenyl)-2,2,2-trichloroethane (DDT),<sup>[7b]</sup> 1,2-migration of a functional group,<sup>[7c]</sup> H<sub>2</sub> production,<sup>[7a]</sup> and alkene reduction.<sup>[7a]</sup> All of these reactions were mediated by the supernucleophilic Co<sup>I</sup> form of B<sub>12</sub> formed by electron transfer from TiO<sub>2</sub> during light irradiation. In general, this type of reaction should be carried out under anaerobic conditions to avoid auto-oxidation of the Co<sup>I</sup> species. Furthermore, active oxygen species are generated by the TiO<sub>2</sub>, which accelerates the decomposition of the modified compound on the TiO<sub>2</sub>.<sup>[6]</sup>

We now report the development of the distinct oxygen-controlled catalysis by B<sub>12</sub>-TiO<sub>2</sub> as shown in Figure 1. Trichlorinated organic compounds were transformed into different products depending on whether the reaction was



**Figure 1.** Oxygen-controlled dechlorination of benzotrichloride by B<sub>12</sub>-TiO<sub>2</sub>.

carried out under N<sub>2</sub> 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.<sup>[9]</sup> The progress of visible-light photoredox catalysts has contributed to a wide range of organic synthesis procedures.<sup>[10]</sup> In our system using a heterogeneous TiO<sub>2</sub> 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.

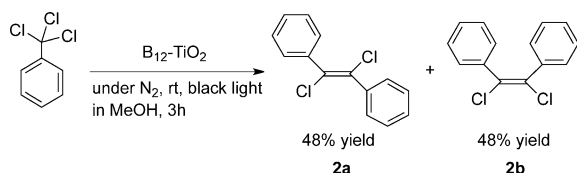
To carry out the aerobic reaction, we newly synthesized a B<sub>12</sub> derivative having two trimethoxysilyl groups and a Co<sup>III</sup> metal center, (CN)<sub>2</sub>Cob<sup>III</sup>6C<sub>1</sub>esterCON{(CH<sub>2</sub>)<sub>3</sub>Si(OMe)<sub>3</sub>}<sub>2</sub> (**1**)

[\*] 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

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <http://dx.doi.org/10.1002/anie.201507782>.

(see the Supporting information), which could be covalently immobilized on the  $\text{TiO}_2$  surface (Figure 1). This  $\text{B}_{12}$  complex is easily and stably bound to the  $\text{TiO}_2$  by mixing with  $\text{TiO}_2$  (anatase, average surface area:  $52 \text{ m}^2 \text{ g}^{-1}$ ) in MeOH at room temperature. The content of the  $\text{B}_{12}$  complex on the surface of  $\text{TiO}_2$  was  $1.37 \times 10^{-5} \text{ mol g}^{-1}$ , and the apparent surface coverage by the  $\text{B}_{12}$  complex was  $2.68 \times 10^{-11} \text{ mol cm}^{-2}$ . This covalently bound  $\text{B}_{12}\text{-TiO}_2$  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  $\text{B}_{12}$  was detected by MALDI-TOF MS owing to its strong binding on the surface of the  $\text{TiO}_2$ , which cannot be desorbed by laser irradiation of the MALDI MS analysis (Figure S8). In contrast,  $\text{B}_{12}$  coordinated to  $\text{TiO}_2$  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  $\text{B}_{12}\text{-TiO}_2$  was more tightly immobilized on  $\text{TiO}_2$  and was a suitable catalyst to perform the aerobic photoreaction. In fact, the covalently bound  $\text{Co}^{\text{III}}$  form of  $\text{B}_{12}$  on the  $\text{TiO}_2$  surface was reduced to  $\text{Co}^{\text{I}}$  from  $\text{Co}^{\text{II}}$  by UV light irradiation with absorption maxima at 390 nm and 470 nm, respectively (Figure S10), which was similar to a previous  $\text{B}_{12}$  (cobyrinic acid)- $\text{TiO}_2$  system.<sup>[7]</sup> Thus, the  $\text{Co}^{\text{I}}$  form of  $\text{B}_{12}$  should react with various organic halides owing to its superelectrophilicity.<sup>[11]</sup>

As for catalytic reactions, we first examined the anaerobic dechlorination of benzotrichloride by  $\text{B}_{12}\text{-TiO}_2$  in MeOH (Supporting information). MeOH was used as a solvent and a hole ( $h_{\text{VB}}^+$ ) consumer of the  $\text{TiO}_2$  valence band. 1,2-Dichlorostilbenes (**2a** and **2b**) were quantitatively formed by UV light irradiation under  $\text{N}_2$  (each 48%; Scheme 1). The



**Scheme 1.** Anaerobic dechlorination of benzotrichloride by  $\text{B}_{12}\text{-TiO}_2$ .

suspended  $\text{B}_{12}\text{-TiO}_2$  catalyst was easily separated by filtration after the reaction. The content of the  $\text{B}_{12}$  complex on the surface of  $\text{TiO}_2$  was  $1.30 \times 10^{-5} \text{ mol g}^{-1}$  after the reaction, and ca. 95 % of  $\text{B}_{12}$  survived during anaerobic reaction. In this way, the covalently bound  $\text{B}_{12}\text{-TiO}_2$  hybrid catalyst also works in the dechlorination of organic halides.

When the reaction was carried out under aerobic conditions (Supporting Information),<sup>[12]</sup> 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).<sup>[13]</sup> 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 ( $h_{\text{VB}}^+$  consumer), the reaction did not proceed (Table 1, entries 3 and 4). The  $\text{B}_{12}$  was also essential for the reaction (Table 1, entries 5 and 6), and the

**Table 1:** Oxidative dechlorination of benzotrichloride to methyl benzoate by  $\text{B}_{12}\text{-TiO}_2$  or other  $\text{TiO}_2$ s.<sup>[a]</sup>

Entry	Catalyst	Time [h]	Atmosphere	Yield [%] <sup>[b]</sup>
1	$\text{B}_{12}\text{-TiO}_2$	3	air	99
2	$\text{B}_{12}\text{-TiO}_2$	5	$\text{O}_2$	91
3	$\text{B}_{12}\text{-TiO}_2$ <sup>[c]</sup>	3	air	0 <sup>[d]</sup>
4	$\text{B}_{12}\text{-TiO}_2$ <sup>[e]</sup>	3	air	trace <sup>[d]</sup>
5	$\text{TiO}_2$	3	air	3
6	$\text{Pt-TiO}_2$ <sup>[f]</sup>	3	air	10
7	$\text{B}_{12}\text{-TiO}_2$ <sup>[g]</sup>	3	air	45

[a]  $[\text{B}_{12}\text{-TiO}_2] = 10 \text{ mg}$  ( $\text{B}_{12}$ ,  $2.28 \times 10^{-5} \text{ M}$ ), [substrate] = 3.0 mm, solvent MeOH 6 mL at room temperature by UV light irradiation (black light,  $\lambda_{\text{max}} = 365 \text{ nm}$ ,  $1.5 \text{ mW cm}^{-2}$  at 10 cm distance). [b] Yield was based on initial concentration of substrate. [c] Dark condition. [d] Most of substrate was recovered. [e] Solvent  $\text{CH}_3\text{CN}$  6 mL was used instead of MeOH. [f]  $\text{Pt-TiO}_2 = 10 \text{ mg}$  (0.15 wt % Pt). [g]  $\text{B}_{12}$  (cobyrinic acid)- $\text{TiO}_2 = 8.7 \text{ mg}$  ( $\text{B}_{12}$ ,  $2.28 \times 10^{-5} \text{ M}$ ).

involvement of reactive oxygen species formed directly by  $\text{TiO}_2$  in the reaction is considered negligible.<sup>[14,15]</sup> The previous  $\text{B}_{12}$ (cobyrinic acid)- $\text{TiO}_2$  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  $\text{B}_{12}$  on  $\text{TiO}_2$ .

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  $h_{\text{VB}}^+$  quencher of  $\text{TiO}_2$ , and the quenching efficiency is correlated with the  $\text{B}_{12}\text{-TiO}_2$  catalytic efficiency.<sup>[16]</sup> In fact, the oxidized product, dimethyl acetal, was obtained in moderate yield as the reaction proceeded.<sup>[17]</sup>

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).<sup>[18]</sup> From 1,1,1-trichloroethane and chloroform, ethyl acetate (**4b**) and ethyl formate (**4c**) were obtained in moderate yields, respectively.<sup>[18]</sup> As for dihalo benzylic compounds, dichloromethyl benzene showed low reactivity for the reaction,<sup>[19]</sup> while dibromomethyl benzene afforded moderate yield of the ester (**3a**).<sup>[20]</sup>

The proposed reaction mechanism is shown in Scheme 3. From the reaction of the  $\text{Co}^{\text{I}}$  species in  $\text{B}_{12}\text{-TiO}_2$ , the dichloromethylbenzene radical (**5**) could be formed from the trichloromethylbenzene. Owing to the electron-withdrawing property of the two chlorine atoms, further reduction by  $\text{TiO}_2$  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

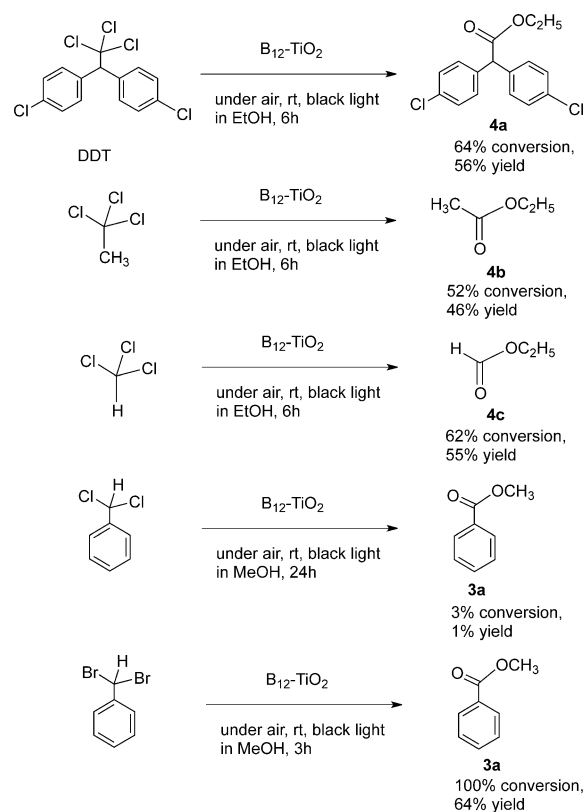
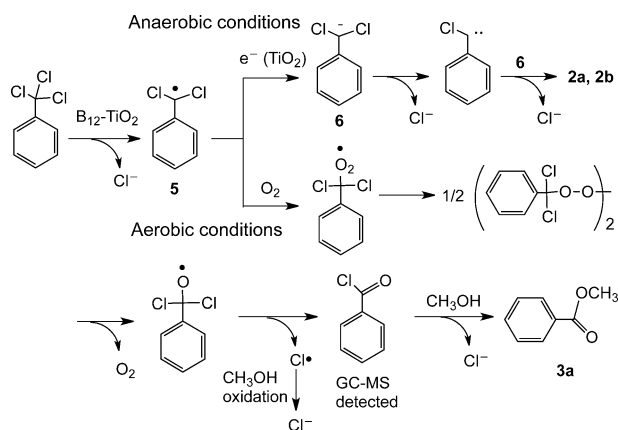
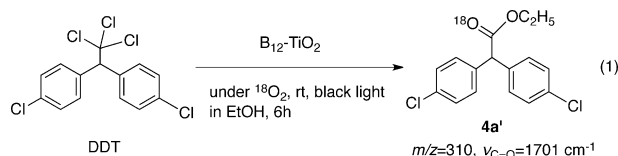
**Table 2:** Oxidative dechlorination of benzotrichloride derivatives by B<sub>12</sub>-TiO<sub>2</sub> under air.<sup>[a]</sup>

Substrate	Product	Yield [%]	Substrate	Product	Yield [%]
		99			87
		99 <sup>[b]</sup>			93
		92 <sup>[c]</sup>			96
		90 <sup>[d]</sup>			99 <sup>[f]</sup>
		10 <sup>[e]</sup>			99 <sup>[f]</sup>
		75			

[a] [B<sub>12</sub>-TiO<sub>2</sub>] = 10 mg (B<sub>12</sub>, 2.28 × 10<sup>-5</sup> M), [substrate] = 3.0 mM, solvent MeOH 6 mL at room temperature by 3 h UV light irradiation (black light, λ<sub>max</sub> = 365 nm, 1.5 mW cm<sup>-2</sup> at 10 cm distance). [b] Solvent = CD<sub>3</sub>OH. [c] Solvent = EtOH. [d] Solvent = *n*-PrOH. [e] Solvent = *i*-PrOH. [f] [substrate] = 1.5 mM, 6 h UV light irradiation.

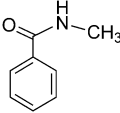
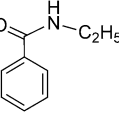
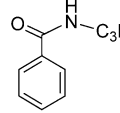
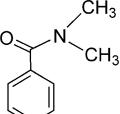
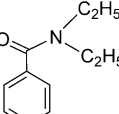
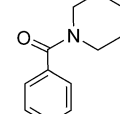
1,1,2,2-tetrachloro-1,2-diphenylethane<sup>[21]</sup> and, following dechlorination, form 1,2-dichlorostilbenes (**2a** and **2b**),<sup>[22]</sup> we could not detect such coupling tetrachloro compounds by GC-MS during the reaction. Thus we have excluded it from the proposed mechanism. While under aerobic conditions, the radical **5** may rapidly react with oxygen to form the peroxy radical.<sup>[23]</sup> The coupling and subsequent elimination of oxygen and disproportionation should form benzoyl chloride as an intermediate.<sup>[24]</sup> 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<sub>3</sub>CN 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 <sup>18</sup>O<sub>2</sub> [Eq. (1)]. In the IR analysis of the ester **4a'**, the ν(ester C=O) peak was shifted to 1701 cm<sup>-1</sup> from 1733 cm<sup>-1</sup> of the authentic ester **4a** (<sup>16</sup>O; Figure S13). In the MS analysis, the parent peak was observed at *m/z* = 310 for **4a'**, while the parent peak for **4a** (<sup>16</sup>O) was observed at *m/z* = 308 (Figure S14). Therefore, it is clear that one <sup>18</sup>O atom was incorporated into the ester as a carbonyl oxygen.<sup>[25]</sup>

Detection of the benzoyl chloride under the aerobic conditions prompted us to develop further applications of the B<sub>12</sub>-TiO<sub>2</sub> catalysis. When the reactions were carried out in the


**Scheme 2.** Scope of the substrate variation.

**Scheme 3.** Proposed reaction mechanism by B<sub>12</sub>-TiO<sub>2</sub> for dechlorination of benzotrichloride.


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

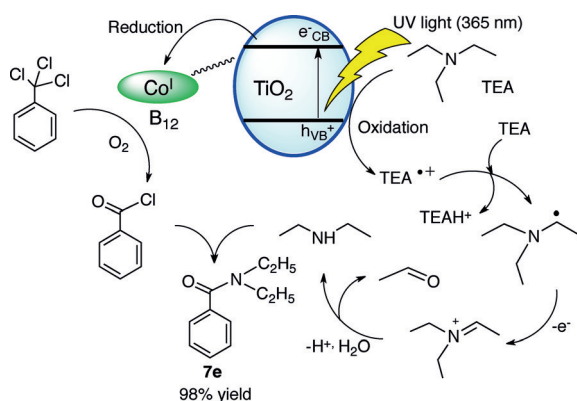
**Table 3:** B<sub>12</sub>-TiO<sub>2</sub> catalyzed amidation of benzotrichloride under air.<sup>[a]</sup>

$\text{C}_6\text{H}_5\text{CCl}_3 \xrightarrow[\text{under air, rt, black light in MeOH, 3h}]{\text{B}_{12}\text{-TiO}_2, \text{ amine (30 equiv. mole to substrate)}} \text{C}_6\text{H}_5\text{C(=O)NHR}$		
 <b>7a</b> 90% yield	 <b>7b</b> 92% yield	 <b>7c</b> 95% yield
 <b>7d</b> 90% yield	 <b>7e</b> 94% yield	 <b>7f</b> 79% yield

[a] [B<sub>12</sub>-TiO<sub>2</sub>] = 10 mg (B<sub>12</sub>,  $2.28 \times 10^{-5}$  M), [benzotrichloride] = 3.0 mM, [amine] = 90 mM, solvent = MeOH 6 mL under air at room temperature by UV light irradiation (black light,  $\lambda_{\text{max}} = 365$  nm,  $1.5 \text{ mWcm}^{-2}$  at 10 cm distance).

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

During the course of this study, we also established a photo-duet reaction (Figure 2; see the Supporting Informa-



**Figure 2.** Photo-duet reaction catalyzed by B<sub>12</sub>-TiO<sub>2</sub>.

tion for further details). Both the reduction and oxidation by the conduction band electron ( $e_{\text{CB}}^-$ ) and  $h_{\text{VB}}^+$  were directly involved in the product formation. The triethyl amine (TEA) quenches  $h_{\text{VB}}^+$  to form the radical cation (TEA<sup>•+</sup>). The sequence reaction of TEA<sup>•+</sup> could produce diethylamine,<sup>[29]</sup> which then reacts with benzoyl chloride to form the amide (**7e**),<sup>[30]</sup> which is a skeleton of chemical insect repellent, *N,N*-diethyl-3-methylbenzamide (DEET).<sup>[31]</sup>

In summary, we have developed for the first time an aerobic molecular transformation by combining B<sub>12</sub> with TiO<sub>2</sub>. The oxygen-controlled catalysis of the B<sub>12</sub>-TiO<sub>2</sub> 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<sub>2</sub>.<sup>[32]</sup>

## Acknowledgements

This study was partially supported by a Grant-in-Aid for Scientific Research (C) (No. 26410122) from the Japan Society for the Promotion of Science (JSPS), and the 2014 Tokuyama Science Foundation.

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

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 15439–15443  
*Angew. Chem.* **2015**, *127*, 15659–15663

- [1] See special reviews for Recoverable Catalysts and Reagents, J. A. Gladysz, *Chem. Rev.* **2002**, *102*, 3215.
- [2] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.
- [3] a) J. Willkomm, N. M. Muresan, E. Reisner, *Chem. Sci.* **2015**, *6*, 2727–2736; b) A. Reynal, F. Lakadamyali, M. A. Gross, E. Reisner, J. R. Durrant, *Energy Environ. Sci.* **2013**, *6*, 3291–3300; c) L. Alibabaei, H. Luo, R. L. House, P. G. Hoertz, R. Lopez, T. J. Meyer, *J. Mater. Chem. A* **2013**, *1*, 4133–4145; d) Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li, L. Sun, *J. Am. Chem. Soc.* **2013**, *135*, 4219–4222; e) J. Huang, K. L. Mulfort, P. Du, L. X. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 16472–16475; f) F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant, E. Reisner, *Chem. Eur. J.* **2012**, *18*, 15464–15475; g) F. Lakadamyali, M. Kato, N. M. Muresan, E. Reisner, *Angew. Chem. Int. Ed.* **2012**, *51*, 9381–9384; *Angew. Chem.* **2012**, *124*, 9515–9518; h) F. Lakadamyali, E. Reisner, *Chem. Commun.* **2011**, 47, 1695–1697.
- [4] a) C. D. Windle, E. Pastor, A. Reynal, A. C. Whitwood, Y. Vaynzof, J. R. Durrant, R. N. Perutz, E. Reisner, *Chem. Eur. J.* **2015**, *21*, 3746–3754; b) K. Sekizawa, K. Maeda, K. Domen, K. Koike, O. Ishitani, *J. Am. Chem. Soc.* **2013**, *135*, 4596–4599.
- [5] a) T. Ito, G. J. Meyer, *Environ. Eng. Sci.* **2007**, *24*, 31–44; b) J. R. Stromberg, J. D. Wnuk, R. A. F. Pinlac, G. J. Meyer, *Nano Lett.* **2006**, *6*, 1284–1286; c) S. O. Obare, T. Ito, G. J. Meyer, *J. Am. Chem. Soc.* **2006**, *128*, 712–733; d) R. J. Kuhler, G. A. Santo, T. R. Caudill, E. A. Betterton, R. G. Arnold, *Environ. Sci. Technol.* **1993**, *27*, 2104–2111.
- [6] See reviews: a) M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341–357; b) M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96; c) A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C* **2000**, *1*, 1–15; d) T. Tachikawa, M. Fujitsuka, T. Majima, *J. Phys. Chem. C* **2007**, *111*, 5259–5275; e) X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891–2959; f) B. Ohtani, *J. Photochem. Photobiol. C* **2010**, *11*, 157–178; g) L. Sang, Y. Zhao, C. Burda, *Chem. Rev.* **2014**, *114*, 9283–9318.
- [7] a) H. Shimakoshi, Y. Hisaeda, *ChemPlusChem* **2014**, *79*, 1250–1253; b) H. Shimakoshi, E. Sakumori, K. Kaneko, Y. Hisaeda, *Chem. Lett.* **2009**, *38*, 468–469; c) H. Shimakoshi, M. Abiru, S. Izumi, Y. Hisaeda, *Chem. Commun.* **2009**, 6427–6429.
- [8] See reviews: a) M. Giedyk, K. Goliszewska, D. Gryko, *Chem. Soc. Rev.* **2015**, *44*, 3391–3404; b) K. Gruber, B. Puffer, B.



- Krätzler, *Chem. Soc. Rev.* **2011**, *40*, 4346–4363; c) W. Buckel, B. T. Golding, *Annu. Rev. Microbiol.* **2006**, *60*, 27–49; d) K. L. Brown, *Chem. Rev.* **2005**, *105*, 2075–2149; e) R. Banerjee, S. W. Ragsdale, *Annu. Rev. Biochem.* **2003**, *72*, 209–247.
- [9] S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran, M. Rueping, *J. Am. Chem. Soc.* **2013**, *135*, 1823–1829.
- [10] See reviews: a) D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176; b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; c) Y. Xi, H. Yi, A. Lei, *Org. Biomol. Chem.* **2013**, *11*, 2387–2403; d) L. Shi, W. Xia, *Chem. Soc. Rev.* **2012**, *41*, 7687–7697; e) T. Koike, M. Akita, *Synlett* **2013**, *24*, 2492–2505; f) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828–6838; *Angew. Chem.* **2012**, *124*, 6934–6944; g) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102–113.
- [11] a) M. Giedyk, S. N. Fedosov, D. Gryko, *Chem. Commun.* **2014**, *50*, 4674–4676; b) H. Shimakoshi, M. Nishi, A. Tanaka, K. Chikama, Y. Hisaeda, *Chem. Commun.* **2011**, *47*, 6548–6550; c) J. E. Argüello, C. Costentin, S. Griveau, J.-M. Savéant, *J. Am. Chem. Soc.* **2005**, *127*, 5049–5055; d) S. Ruppe, A. Neumann, G. Diekert, W. Vetter, *Environ. Sci. Technol.* **2004**, *38*, 3063–3067; e) D.-L. Zhou, C. K. Njue, J. F. Rusling, *J. Am. Chem. Soc.* **1999**, *121*, 2909–2914; f) G. Glod, W. Angst, C. Holliger, R. P. Schwarzenbach, *Environ. Sci. Technol.* **1997**, *31*, 253–260; g) U. E. Krone, R. K. Thauer, H. P. C. Hogenkamp, *Biochemistry* **1989**, *28*, 4908–4914; h) A. Fischli, J. J. Daly, *Helv. Chim. Acta* **1980**, *63*, 1628–1643; i) R. Scheffold, E. Amble, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 629–630; *Angew. Chem.* **1980**, *92*, 643–644; j) G. N. Schrauzer, E. Deutsch, *J. Am. Chem. Soc.* **1969**, *91*, 3341–3350.
- [12] Concentrations of oxygen in MeOH are estimated from the literature,  $[O_2]_{air} = 2.2$  mM.  $[O_2]_{O_2} = 10.3$  mM, M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, In *Handbook of Photochemistry*, 3<sup>rd</sup> ed., Taylor & Francis, New York, **2006**, p. 546.
- [13] In contrast to the anaerobic reaction,  $B_{12}$  on the  $TiO_2$  was gradually decomposed after the aerobic reaction, and turnover number of  $B_{12}$  for **3a** formation was 130. When the  $B_{12}$ - $TiO_2$  catalyst was decreased to 1/10 (1 mg), yield of **3a** was 46% after 3 h UV irradiation and turnover number of  $B_{12}$  was 460.
- [14] a) T. Daimon, T. Hirakawa, M. Kitazawa, J. Suetake, Y. Nosaka, *Appl. Catal. A* **2008**, *340*, 169–175; b) V. Brezová, S. Gabcová, D. Dvoranová, A. Stasko, *J. Photochem. Photobiol. B* **2005**, *79*, 121–134; c) R. Konaka, E. Kasahara, W. C. Dunlap, Y. Yamamoto, K. C. Chien, M. Inoue, *Free Radical Biol. Med.* **1999**, *27*, 294–300.
- [15] Furthermore, **3a** formation by the  $B_{12}$ - $TiO_2$  was not repressed by singlet oxygen quenchers such as  $\beta$ -carotene or 1,5-dihydroxynaphthalene (see the Supporting information).
- [16] The rates and yields of the photocatalytic oxidation of alcohols on  $TiO_2$  were evaluated, see: Y. Tamaki, A. Furube, M. Murai, K. Hara, R. Katoh, M. Tachiya, *J. Am. Chem. Soc.* **2006**, *128*, 416–417.
- [17] It is considered that oxidation of alcohol by  $h^+$  produces aldehyde and proton. This proton could compensate negative charge of chloride anion removed from benzotrichloride. The remaining aldehyde reacts with alcohol to form acetal by acid catalysis (Ref. [7c]). Yield of dimethyl acetal was almost similar to that of the product under  $N_2$ , while it was in excess to that of the ester under air owing to waste of  $e_{CB}^-$  by reduction of  $O_2$ .
- [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.
- [19] Trace amounts of benzaldehyde and benzaldehyde dimethyl acetal were formed.
- [20] Benzaldehyde and benzaldehyde dimethyl acetal were also formed with 19% and 13% yields, respectively.
- [21] S. A. Kaufman, T. Phanijphand, A. J. Fry, *Tetrahedron Lett.* **1996**, *37*, 8105–8108.
- [22] In the separate photoreaction (black light,  $\lambda_{max} = 365$  nm,  $1.5$  mW cm<sup>-2</sup> at 10 cm distance), dechlorination of 1,1,2,2-tetrachloro-1,2-diphenylethane (2 mM) by  $B_{12}$ - $TiO_2$  (10 mg) under nitrogen in 6 mL MeOH produced **2a** and **2b** with 38% and 60% yields, respectively.
- [23] a) P. Neta, R. E. Huie, A. B. Ross, *J. Phys. Chem. Ref. Data* **1990**, *19*, 413–513; b) J. Wilshire, D. T. Sawyer, *Acc. Chem. Res.* **1979**, *12*, 105–110.
- [24] a) S. Yamazaki, T. Tanimura, A. Yoshida, K. Hori, *J. Phys. Chem. A* **2004**, *108*, 5183–5188; b) C. von Sonntag, H.-P. Schuchmann, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1229–1253; *Angew. Chem.* **1991**, *103*, 1255–1279 c) J. E. Bennett, J. A. Howard, *J. Am. Chem. Soc.* **1973**, *95*, 4008–4010.
- [25] We also quantified the number of  $Cl^-$  after the reaction by the spectrophotometric determination using the mercury(II) thiocyanate method (Ref. [26]). In the case of benzotrichloride, 2.9 equivalent mole of  $Cl^-$  was detected under aerobic reaction. Owing to its strong oxidizing ability  $E(Cl^+/Cl^-) = 2.4$  V vs. NHE,<sup>[27]</sup> one  $Cl^-$  could be reduced to  $Cl^-$  by solvent methanol (Scheme 3).
- [26] T. M. Florence, Y. J. Farrar, *Anal. Chim. Acta* **1971**, *54*, 373–377.
- [27] D. O. Mártire, J. A. Rosso, S. Bertolotti, G. C. L. Roux, A. M. Braun, M. C. Gonzalez, *J. Phys. Chem. A* **2001**, *105*, 5385–5392.
- [28] Small amounts of methyl benzoate (4–10%) were formed in each reaction.
- [29] B. Probst, A. Rodenberg, M. Guttentag, P. Hamm, R. Alberto, *Inorg. Chem.* **2010**, *49*, 6453–6460.
- [30] To complete the reaction, 30 equiv mole of TEA was required owing to waste of  $e_{CB}^-$  by reduction of  $O_2$  (see the Supporting information).
- [31] M. S. Fradin, J. F. Day, *N. Engl. J. Med.* **2002**, *347*, 13–18.
- [32] See reviews: a) J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.* **2014**, *114*, 9919–9986; b) R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *Chem. Rev.* **2014**, *114*, 9824–9852.

Received: August 19, 2015

Revised: October 9, 2015

Published online: November 3, 2015