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ARTICLE TYPE

Electrolysis of Trichloromethylated Organic Compounds under Aerobic Conditions Catalyzed by B_{12} Model Complex for Ester and Amide Formations[†]

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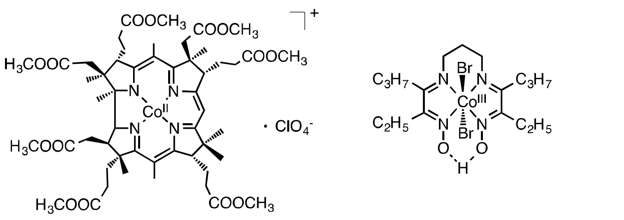
The electrolysis of benzotrichloride at -0.9 V *vs*. Ag/AgCl in the presence of the B_{12} model complex, heptamethyl cobyrinate perchlorate, in ethanol under aerobic conditions using an undivided cell equipped with a platinum mesh cathode and zinc plate anode produced ethylbenzoate in 56% yield with a 92% selectivity. The corresponding esters were obtained when the electrolysis was carried out in various alcohols such as methanol, *n*-propanol, and *i*-propanol. Benzoyl chloride was detected by GC-MS during the electrolysis as an intermediate for the ester formation. When the electrolysis was carried out under anaerobic conditions, partially dechlorinated products, 1,1,2,2-tetrachloro-1,2-diphenylethane and 1,2-dichlorostilibenes (*E* and *Z* forms) were obtained instead of an ester. ESR spin-trapping experiments using 5,5,-dimethylpyrroline *N*-oxide (DMPO) revealed that the corresponding oxygen-centered radical and carbon-centered radical were steadily generated during the electrolyses under aerobic and anaerobic conditions, respectively. Applications of the aerobic electrolysis to various organic halides, such as substituted benzotrichlorides, are described. Furthermore, the formations of amides with moderate yields by the aerobic electrolysis of benzotrichloride catalyzed by the B_{12} model complex in the presence of amines in acetonitrile are reported.

1. Introduction

Reductive dehalogenations of organic halides have been extensively studied for a long time primary because of remedial approaches to remove such chemicals, ex. halogenated solvent wastes, from contaminated soils or rivers by treatment with chemical reductants.[1] The reductive dehalogenation of organic halides also developed in synthetic organic chemistry since activation of the carbon-halogen bond of organic halides to afford carbon-centered radicals that is a useful intermediate in organic synthesis.[2] To achieve the reaction, a variety of methods was developed over decades such as using a photosensitizer[3] or microwave irradiation[4] other than conventional chemical treatment with a reductant. Among the methods, electrochemical techniques were extensively studied in this field[5] since the redox process of the substrate occurs by an electric current without a chemical reagent and waste after the reaction. Therefore, electrochemical methods are recognized as green processes both in the laboratory and industrial chemistry, and currently expanding into various interdisciplinary fields.[6] For the electrolysis of organic halides, indirect electrolysis using a mediator provides a further advantage for the reaction.[7] For example, electrolysis proceeds at a more positive potential than that of direct electrolysis at the cathode. Furthermore, an electrochemically generated low-valent metal complex like the Co(I) species can attack an organic halide by a nucleophilic reaction which expands the scope of the substrate.[8]

As for the cobalt complex, a variety of tetracoordinated complexes were utilized for the reaction such as cobalt porphyrins,[9] cobalt phtalocyanines,[10] cobalt schiff-base complexes,[11] cobalt cyclams[12], etc. Cobalamin derivatives that emerged in the active site of the B_{12}-dependent enzyme[13] have been widely used in the electrolysis of organic halides as well as the model reactions of B_{12}-dependent enzymes.[14] Since the Co(I) species of the cobalamine derivatives have a high reactivity to organic halides with a supernucleophilicity,[15] the dehalogenation of organic halides, such as haloacetic acids,[16] CCl_4,[17] FREONs,[17b] tetrachloroethylene,[18] trichloroethylene,[18] 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT),[19] and 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD)[19] were reported. For a such reductive reaction, electrolysis should be carried out under anaerobic conditions since the labile Co(I) species rapidly reacts with oxygen to oxidize to Co(II) or Co(III) which causes loss of the electric charge during the electrolysis. Recently, we found that the Co(I) species of B_{12} derivative generated by electron transfer from TiO_2 by UV light irradiation catalyzed the oxidative dechlorination of trichloromethylated organic compounds to form esters under aerobic conditions.[20] Though the competing reaction of the Co(I) species with oxygen over the organic halide lowers the reaction efficiency, the reaction between oxygen and the carbon-centered radical generated by the reductive dechlorination of the organic halide formed a new strategy for molecular transformation.

We now demonstrate this strategy for the reductive electrolysis of an organic halide under aerobic conditions catalyzed by the B_{12} model complex (**1**), heptamethyl cobyrinate perchlorate (Fig. 1). A variety of esters were formed from benzotrichloride by a one-pot electrolysis in various alcohols, and amides were also obtained in the presence of amines by aerobic electrolysis catalyzed by the B_{12} model complex.



B_{12} model complex (**1**) $[Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2]$ (**2**)

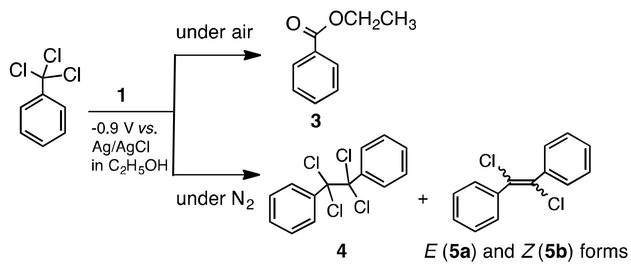


Figure 1. Electrolyses of benzotrichloride catalyzed by B_{12} model complex (**1**) under air or N_2 in ethanol.

2. Experimental

2.1 Materials

The solvents and chemicals used in the syntheses were of reagent grade and used without further purification. Solvents for the electrolysis were of spectral grade purchased from WAKO. Tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) was purchased from Nakalai Chemicals (special grade) and dried at room temperature under vacuum before use. Heptamethyl cobyrinate perchlorate (**1**) (Fig. 1) was synthesized by a previously reported method.[21] The cobalt complex, $[Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2]$, $(C_2C_3)(DO)(DOH)pn$ is 4,10-dipropyl-5,9-diazatrideca-4,9-diene-3,10-dione dioxime), (**2**) (Fig. 1) was prepared according to the literature.[22]

2.2 Characterization

Elemental analyses for C, H and N were obtained from the Service Center of Elementary Analysis of Organic Compounds at Kyushu University. The NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis of Kyushu University. The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The MALDI-TOF mass spectra were obtained by a Bruker autoflex II using 6-aza-2-thiothymine as the matrix. Gel permeation chromatography (GPC) was carried out by a Japan Analytical Industry Co. Ltd., LC-908 apparatus equipped with a UV-3702 attachment using three connected columns, JAIGEL-1H, 2H, and 2.5 H with a $CHCl_3$ eluent. The GC-mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μm). The cyclic voltammograms (CV) were obtained using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with 1.6-mm diameter platinum wires as the working and counter electrodes was used. An Ag/AgCl (3.0 M NaCl) electrode served as the reference. The $E_{1/2}$ value of the ferrocene-ferrocenium (Fc/Fc^+) was 0.46 V *vs*. Ag/AgCl with this setup.

2.3 General bulk electrolysis

The controlled-potential electrolysis of benzotrichloride was carried out in a one-compartment cell equipped with a Pt mesh or a carbon felt cathode and a zinc plate anode (1x3 cm^2) at -0.9 V *vs*. Ag/AgCl in the presence of **1** at room temperature in 0.1 M n-Bu_4NClO_4 containing ethanol. The zinc electrode was used as a sacrificial anode. The applied potential between the working and reference electrodes in the electrolysis was maintained constant using a Hokuto Denko HA BF-501A potentiostat, and the electrical quantity was also recorded by it. The concentrations of the catalyst and substrate were $5.0x10^{-4}$ M and $5.0x10^{-2}$ M, respectively. During the electrolysis, ethanol-saturated air was bubbled using a Teflon tube. To carry out the electrolysis under anaerobic conditions, the electrolysis was carried out in glovebox, mBRAUN UNIlab, with N_2 atmosphere (O_2<1ppm). After the electrolysis, the electrolyte solution was passed through silica gel with the $CHCl_3$ eluent, then analyzed by GC-MS. Authentic samples of the anaerobic and aerobic products from the catalytic reactions (**3-16** except for **5b**) (Tables 1-3) were purchased from Aldrich or Tokyo Kasei Kogyo (TCI). The anaerobic product **5b** was isolated by GPC and characterized by elemental analysis, GC-MS, NMR, and compared to reported values.[23]

5b: ^1H NMR ($CDCl_3$): δ 7.22 (m, 10H, Ph), ^{13}C NMR ($CDCl_3$): δ 137.6, 131.2, 130.1, 129.0, 128.5, GC-MS, *m/z*: $[M]^+$=248. Found: C, 67.05; H, 4.08. Calc. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05%.

2.4 Spin-trapping experiment by ESR

The ESR spectra were obtained using a Bruker EMX-Plus X-band spectrometer at room temperature. The ESR spectra for the DMPO spin-trapping products were observed during the electrolysis of benzotrichloride ($5.0x10^{-2}$ M) in the presence of DMPO ($2.5x10^{-1}$ M) and **1** ($5.0x10^{-4}$ M) in ethanol under air or nitrogen. The settings for the ESR measurements were a frequency of 9.87 GHz, power of 1.0 mW, center field of 3515 G, sweep width of 150 G, modulation amplitude of 3.0 G, time constant of 40 ms, and sweep time of 20 s.

2.5 Quantification of chloride ion

The chloride ions removed from the benzotrichloride by electrolysis under aerobic condition was quantified using the mercury (II) thiocyanate method.[24] After the electrolysis, 30 μL of the electrolyte solution was added to 2 mL of carbontetrachloride, then 1 mL of water was added to extract the chloride ion. The procedure was repeated two times and the chloride ion in the aqueous solution was quantified by UV-vis spectroscopy (Fig. S1, ESI†).

3. Results and discussion

The redox behavior of heptamethyl cobyrinate perchlorate (**1**) under anaerobic conditions was investigated in detail.[14b, 25] The

CV of **1** in ethanol under nitrogen is shown in Fig. 2a. A reversible Co(II)/Co(I) redox couple was observed at -0.58 V. *vs*. Ag/AgCl. The addition of an excess of benzotrichloride changed the voltammetric pattern and gave rise to a new irreversible redox wave at ca. -0.7 V *vs*. Ag/AgCl as shown in Fig. 2b, which is conventionally ascribed to the reduction of the alkylated complex of **1**.[15b, 19] When the same CV was measured in air, the reduction wave of oxygen observed at around ca. -0.7 V *vs*. Ag/AgCl covered the wave of the Co(II)/Co(I) couple as shown in Fig. 3a. Though the oxygen reduction wave was still observed around ca. -0.6 V *vs*. Ag/AgCl, distinct reductive current was observed at -0.5 V ~ -1.0 V *vs*. Ag/AgCl in the presence of benzotrichloride as shown in Fig. 3b. This catalytic current might be ascribed to the Co(II)/Co(I) and $PhCCl_2$-Co(III)/($PhCCl_2$-Co(III))$^{\cdot-}$ redox couples. Therefore, two catalytic cycles for the benzotrichloride reduction mediated by **1** are possible as shown in Fig. 4.

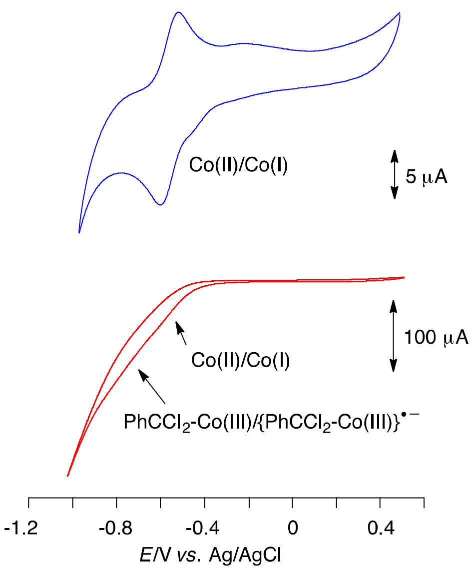


Figure 2. CVs of **1** (1 mM) in ethanol containing 0.1 M n-$Bu_4N_4ClO_4$ under N_2 (blue); and in the presence of benzotrichloride (10 mM) (red).

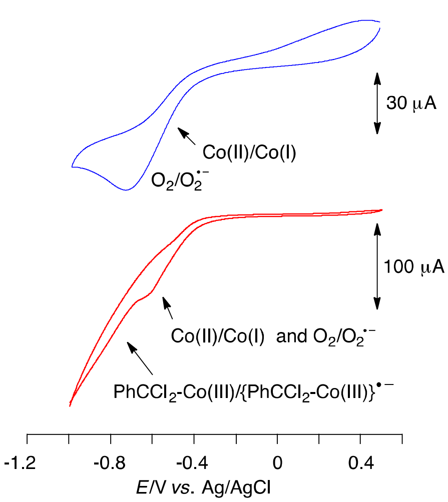


Figure 3. CVs of **1** (1 mM) in ethanol containing 0.1 M n-$Bu_4N_4ClO_4$ under air (blue); and in the presence of benzotrichloride (10 mM) (red).

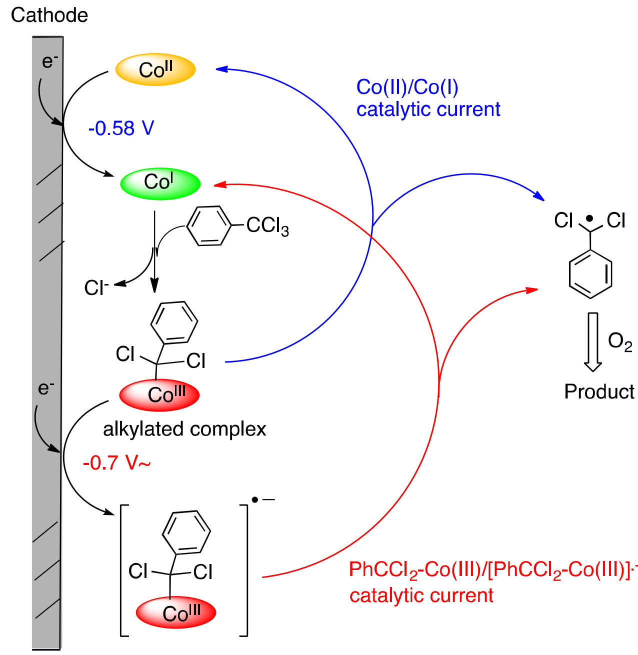
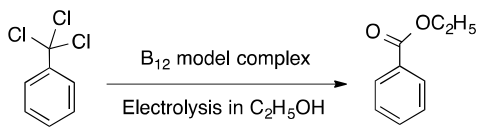


Figure 4. Expected catalytic cycles for electrolysis of benzotrichloride catalyzed by **1**.

The controlled-potential electrolyses were carried out in ethanol and the results are summarized in Table 1. When the electrolysis was carried out at -0.9 V *vs*. Ag/AgCl under air, ethylbenzoate (**3**) was obtained in 56% yield with small amounts of dimers, i.e., 1,1,2,2-tetrachloro-1,2-diphenylethane (**4**), (*E*)- and (*Z*)-1,2-dichlorostilbenes (**5a**, **5b**), with 92% selectivity (Entry 1 in Table 1). When the electrolysis was carried out under nitrogen (in the glovebox, O_2<1 ppm), almost all of the benzotrichloride was consumed after the 3h electrolysis but formation of the ester **3** was completely inhibited and partially dechlorinated products, dimers (**4**, **5a**, **5b**), were obtained (Entry 3 in Table 1). In contrast, too much oxygen disturbed the reaction and the conversion of benzotrichloride was only 10% after the 3h electrolysis since oxygen may quench the Co(I) species (Entry 2 in Table 1).[‡] Without a catalyst, the reaction did not proceed under the same conditions (Entry 4 in Table 1). This suggests that the electrogenerated superoxide ion does not take part in the dechlorination of benzotrichloride in this reaction system, different from previously reported ones.[26] When the electrolysis was conducted at -1.8 V *vs*. Ag/AgCl without a catalyst under air, direct reduction of the benzotrichloride[§] formes **3** (8%), while dichloromethylbenzene (19%) and 1,1,2,2-tetrachloro-1,2-diphenylethane (**4**) (2%) were formed (Entry 5 in Table 1). Upon the addition of DMPO, the formation of the products was inhibited (Entry 6 in Table 1). Therefore, it was expected that some radical intermediates existed an intermediates for product formation. The imine/oxime type cobalt complex (**2**),[¶] [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2] (Fig. 1), which is a well-known functional model compound of B_{12} showed a low reactivity (Entry 7 in Table 1), probably due to its low stability under aerobic electrolysis conditions. The B_{12} model complex **1** is a tough and excellent catalyst for the reaction. The reaction proceeded using inexpensive carbon felt electrode instead of Pt mesh (Entry 8 in Table 1). It is noted that the present electrochemical method has some characteristics and advantages for reaction compare to photocatalytic system using TiO_2 as photosensitizer.[20] (1) Scale-up for reaction is more easy and concentration of substrate was 17 times larger than the previous photocatalytic system. (2) B_{12} catalyst could be decreased by using B_{12}-modified electrode.[27] (3) Reaction proceeds under mild condition in contrast to photocatalytic system which requires UV light irradiation.

Table 1. Electrolysis of benzotrichloride catalyzed by B_{12} model complex (**1**) in C_2H_5OH.[a]



3

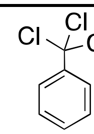
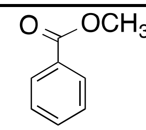
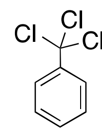
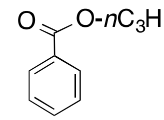
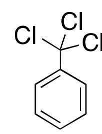
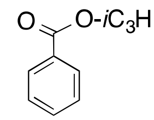
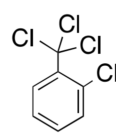
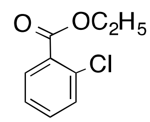
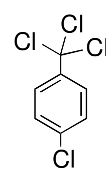
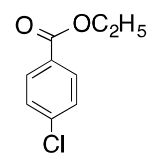
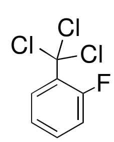
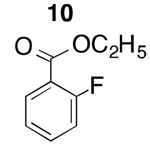
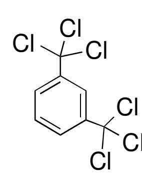
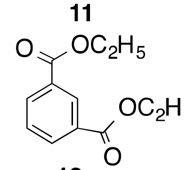
Entry	Atomosphere	Catalyst	Conversion (%)	Yield of **3** (%)	Yield of **4** (%)	Yield of **5a**, **5b** (%)
1	air	**1**	61	56	Trace	Trace, 5
2	O_2	**1**	10	8	0	0
3	N_2	**1**	95	0	1	15, 72
4	air	None	3	0	Trace	0
5[b]	air	None	33	8	2	0
6[c]	air	**1**	94	3	3	7, 25
7	air	**2**	8	2	0	0, Trace
8[d]	air	**1**	55	48	1	Trace, 1

[a] Conditions: [cobalt complex] = 5×10^{-4} M; [benzotrichloride] = 5×10^{-2} M; [n-Bu_4NClO_4] = 1×10^{-1} M using Pt mesh cathode at room temperature. Applied potentials were -0.9 V *vs*. Ag/AgCl for 3h. Conversion of benzotrichloride and the yield of product were based on initial concentration of the substrate. [b] Applied potentials were -1.8 V *vs*. Ag/AgCl. Dichloromethylbenzene was formed at 19% yield. [c] In the presence of DMPO, 0.75 M. [d] Carbon felt cathode.

The aerobic electrolysis for the formation of an ester was applied to other substrates, i.e., benzotrichloride derivatives, or in other alcohols to form the corresponding esters as shown in Table 2. When the reactions were carried out in methanol or n-propanol, methyl benzoate (**6**) or n-propyl benzoate (**7**) was obtained in moderate yields, respectively (Entries 1 and 2 in Table 2). In contrast, in i-propanol, only a 14% yield of i-propyl benzoate (**8**) was obtained (Entry 3 in Table 2). The benzotrichloride derivatives showed moderate product yields (Entries 4-7 in Table 2). Note that the formation of aldehydes or ketones via the reduction of alkyl halides by electrogenerated nickel (I) or cobalt (I) salen in the presence of oxygen was reported by Peters *et al*.[28] The electrolysis of organic halides in the presence of oxygen catalyzed by a metal complex will be an attractive method in electroorganic chemistry.

To elucidate the mechanism, ESR spin-trapping experiments were conducted using DMPO as the radical trap under aerobic and anaerobic conditions. The ESR signal for the carbon-centered radical trapped DMPO (g=2.008, A_N=15.0 G, A_H=21.7 G) was observed during the electrolysis of benzotrichloride in the presence of **1** under nitrogen as shown in Fig. 5a. The hyperfine coupling constants were consistent with those for the reported carbon-centered radical trapped DMPO (A_N =14-16 G, A_H =22-23 G).[29] While the electrolysis of benzotrichloride was carried out in air in the presence of **1**, the ESR signal for the oxygen-centered radical trapped DMPO (g=2.010, A_N=13.4 G, A_H=7.6 G) was observed as shown in Fig. 5b and ester formation was inhibited as shown by entry 6 in Table 1. We may distinguish oxyl-radical adduct (A_H=6.6~9.6) from peroxyl-radical adduct (A_H=10~12.6) by A_H value.[29] Similar ESR spectrum was obtained during electrolysis of 4-chloro-benzotrichloride under air (Fig. S2, ESI†).

Table 2. Electrolysis of benzotrichloride derivatives catalyzed by B_{12} model complex (**1**) in various alcohols under air.[a]

Entry	Substrate	Product	Yield of ester (%)
1		 **6**	52
2		 **7**	33
3		 **8**	14
4		 **9**	48
5		 **10**	47
6		 **11**	48
7[b]		 **12**	85

[a] Conditions: [**1**] = 5×10^{-4} M; [substrate] = 5×10^{-2} M; [n-Bu_4NClO_4] = 1×10^{-1} M at room temperature. Applied potentials were -0.9 V *vs*. Ag/AgCl. Conversion of substrate and the yield of product were based on initial concentration of the substrate. [b] [substrate] = 2.5×10^{-2} M.

Based on these results, the plausible reaction mechanism is shown in Fig. 6. By the reaction of the Co(I) species generated by the electrolysis at -0.9 V *vs.* Ag/AgCl, the dichloromethylbenzene radical (**A**) could be formed from the substrate benzotrichloride. Under the applied potential condition at -0.9 V *vs.* Ag/AgCl at room temperature, the intermediated alkylated complex should be thermally or electrochemically decomposed (Fig. 4).‖ The coupling of radical **A** may produce 1,1,2,2-tetrachloro-1,2-diphenylethane (**4**). Further reductive dechlorination of **4** catalyzed by **1** will produce **5a** and **5b**.# Actually, the electrolysis of **4** at -0.9 V vs. Ag/AgCl in the presence of **1** in nitrogen produced **5a** and **5b** with 11% and 47% yields, respectively (ESI†).

While under aerobic conditions, the radical **A** may rapidly react with oxygen to form the peroxy radical.[30] The coupling and subsequent elimination of oxygen and disproportionation should form benzoyl chloride as an intermediate.[20, 31] The benzoyl chloride could react with the solvent alcohol to form the ester. The formation of the benzoyl chloride was also confirmed by GC-MS during the electrolysis of benzotrichloride in air in anhydrous CH_3CN in which the benzoyl chloride more stably existed than in the alcohol solvent system (Fig. S3, ESI†). We also quantified the number of chloride ions after the reaction by spectrophotometric determination using the mercury(II) thiocyanate method.[24] In the case of benzotrichloride, 2.9 equivalent moles of chloride ion was detected during the aerobic reaction (Fig. S1, ESI†). Due to its strong oxidizing ability for $E(Cl^{\cdot}/Cl^{-})$=2.4 V *vs.* NHE,[32] one chlorine radical could be reduced to a chloride ion by alcohol solvent as shown in Fig. 6.

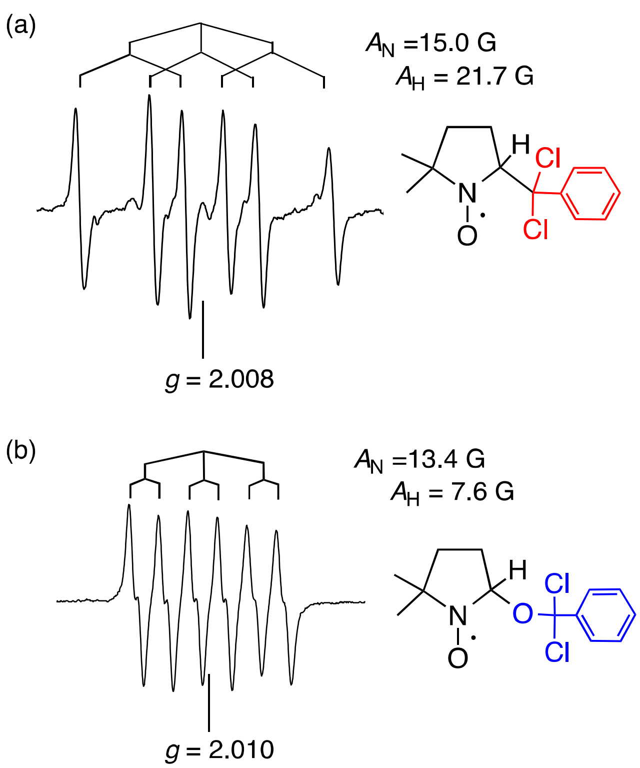


Figure 5. ESR spectra observed during the electrolysis at -0.9 V *vs.* Ag/AgCl in ethanol; [**1**]=5×10^{-4} M; [benzotrichloride]=5.0×10^{-2} M; [DMPO]=2.5×10^{-1} M; [n-Bu_4NClO_4]=1.0×10^{-1} M under N_2 (a) and air (b).

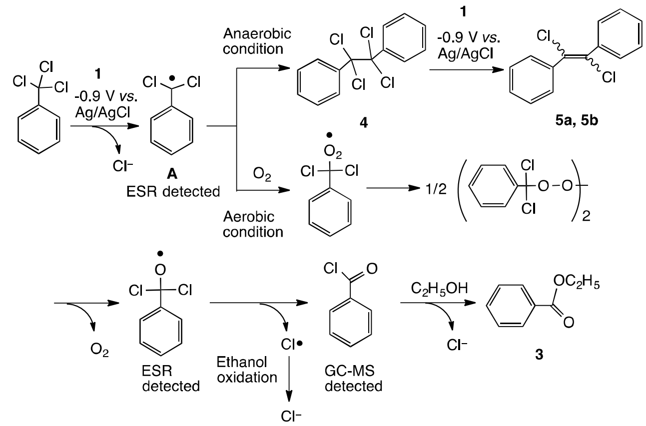
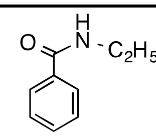
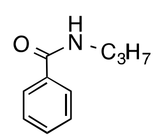
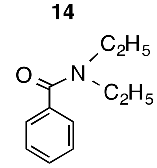
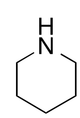
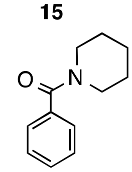


Figure 6. Proposed reaction mechanisms for electrolyses of benzotrichloride catalyzed by **1** under aerobic/anaerobic conditions.

Detection of the benzoyl chloride under aerobic conditions prompted us to develop a further application of the aerobic electrolysis for other fine chemical syntheses. When the electrolysis was carried out in the presence of amines (10 equiv. mole toward substrate), the corresponding amides (**13**-**16**) were produced in place of the ester as shown in Table 3. As the acyl halides are intermediate for various organic compounds, the aerobic electrolysis could be applied to many organic syntheses.

Table 3. Electrolysis of benzotrichloride catalyzed by B_{12} model complex (**1**) in the presence of amines in acetonitrile under air.[a]

Entry	Amine	Product	Yield of amide (%)
1	$CH_3CH_2NH_2$	 **13**	40
2	$CH_3CH_3CH_2NH_2$	 **14**	43
3	$(C_2H_5)_2NH$	 **15**	55
4		 **16**	54

[a] Conditions: [**1**] = 5×10^{-4} M; [benzotrichloride] = 5×10^{-2} M; [amine] = 5×10^{-1} M; [n-Bu_4NClO_4] = 1×10^{-1} M at room temperature in acetonitrile. Applied potentials were -0.9 V *vs.* Ag/AgCl. Conversion of benzotrichloride and the yield of product were based on initial concentration of benzotrichloride.

4. Conclusion

In summary, the aerobic electrolyses of trichloromethylated organic compounds catalyzed by the B_{12} model complex in alcohol produced esters with a high selectivity. The mechanism for the ester formation was investigated by several experiments. Benzoyl chloride was the key intermediate for the reaction. Application of the aerobic electrolysis of benzotrichloride for amide synthesis was also reported. Further applications of the method for other fine chemicals syntheses catalyzed by the B_{12} catalyst is currently in progress in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Figure S1-S2]. See DOI: ##########.

‡ The concentrations of oxygen in ethanol at 298 K are estimated from the literature, $[O_2]_{air}$=2.1 mM. $[O_2]_{O2}$=9.92 mM, M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, in *Handbook of Photochemistry, 3rd ed., Taylor&Francis,* 2006.

§ The E_{pc} of benzotrichloride was reported as -1.65 V *vs.* Ag/AgCl in acetonitrile. M. Borsari, D. Dallari, C. Fontanesi, G. Gavioli, D. Iarossi, R. Piva, F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1839.

¶ The $E_{1/2}$ for Co(II)/Co(I) redox couple of **2** was observed at -0.5 V *vs.* Ag/AgCl in ethanol.

‖ Previously, we could detect dichloroalkyl-cobalt complex of **1** from $CHCl_3$ (H. Shimakoshi *et al*, *Bull. Chem. Soc. Jpn*., 2005, **78**, 859). In contrast, coresponding dichloroalkyl-cobalt complex of **1** was not detected by UV-vis spectroscopy during electrolysis of benzotrichloride under N_2 but observed spectrum for Co(II) species of **1** (Fig. S4, ESI†). This is probably due to steric hindrance of dichlorobenzyl group in the alkylated-cobalt complex that may causes destabilization of cobalt-carbon bond in the complex. Furthermore, the dichlorobenzyl-cobalt complex should be reduced to decompose at -0.9 V *vs.* Ag/AgCl.

Due to the electron-withdrawing property of the two chlorine atoms in **A**, the following mechanism is posiible for 1,2-dichlorostilbene (**5a**, **5b**) formation. The reduction of **A** may produce the carbanion intermediate (**B**) under anaerobic conditions, and the carbanion **B** may lead to a carbene species **C** with elimination of the chloride ion. The electrophilic carbene may react with the carbanion **B** to form **5a** and **5b**.

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