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Hydrophobic vitamin B_{12}. Part 19:† Electroorganic reaction of DDT mediated by hydrophobic vitamin B_{12}

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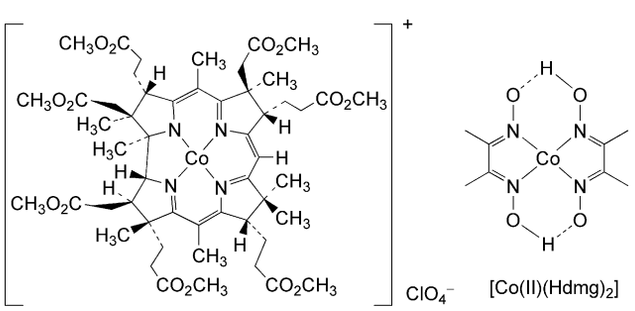
The controlled-potential electrolysis of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (**DDT**) was carried out at −1.4 V *vs.* Ag–AgCl in the presence of a hydrophobic vitamin B_{12}, heptamethyl cobyrinate perchlorate. **DDT** was dechlorinated to form 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (**DDD**), 1,1-bis(4-chlorophenyl)-2,2-dichloroethylene (**DDE**), 1-chloro-2,2-bis(4-chlorophenyl)ethylene (**DDMU**) and 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene (**TTDB**) (*E*/*Z*), and quantitative recovery of the catalyst after the electrolysis was confirmed by electronic spectroscopy. A photo-sensitive intermediate having a cobalt–carbon bond formed during the electrolysis was characterized by electronic spectroscopy. A mechanism for the formation of various dechlorinated products was investigated by using deuterium solvents and various spectroscopic measurements such as UV-VIS and the EPR spin-trapping technique.

Introduction

Reductive dehalogenation reactions are presently of great interest, primarily because of their potential use in the treatment of halogenated solvent wastes as well as in remedial approaches to removing such chemicals from contaminated soils.[1] Recently, it has been demonstrated that certain bacteria can use tetrachloroethane as electron acceptors by reducing it to *cis*-dichoroethane.[2,3] The enzyme *reductive dehalogenase* contains cobalamin as cofactor.[2,3] A Co(I) species of cobalamin is a supernucleophile and reacts with an alkyl halide to form an alkylated complex with dehalogenation.[4–6] The ability of cobalamin for reductive dehalogenation prompted us to investigate the catalysis of a cobalamin derivative for degradation of various halogenated organic compounds.

We have been dealing with a hydrophobic vitamin B_{12}, heptamethyl cobyrinate perchlorate [Cob(II)7C_1ester]ClO_4, which has ester groups in place of the peripheral amide moieties of the naturally occurring cobalamin as shown in Chart 1,[7] and performed various enzymic reactions, mainly isomerization reactions leading to the intramolecular exchange of a functional group and a hydrogen atom, using hydrophobic vitamin B_{12} derivatives as catalysts.[8–13] In the course of these studies, hydrophobic vitamin B_{12} derivatives were found to act as excellent model compounds for the functional simulation of cobalamin-dependent enzymes.



[Cob(II)7C_1ester]ClO_4
(Hydrophobic vitamin B_{12})

[Co(II)(Hdmg)$_2$]

Chart 1

Among the reported methods for dehalogenation of chlorinated organic compounds,[1,14–16] the electrochemical method has various advantages, such as cleanness and energy efficiency, and is proved to be an excellent approach for degradation of various halogenated organic compounds. The direct reductive dehalogenation reactions of chlorinated organic compounds has been reported by several groups.[17,18] Peters and co-workers[19] and Rusling and co-workers[20] reported indirect electrolysis of halogenated organic compounds using a cobalt complex as mediator. Electron-transfer mediators can cleave the carbon–halogen bond at a more positive potential than that required for direct reduction of the carbon–halogen bond. In connection with such study, Keese and co-workers reported the electrolysis of trichlorotoluene catalyzed by [Cob(II)7C_1ester]ClO_4.[21] Recently, we also reported dehalogenation of benzyl bromide and phenethyl bromide catalyzed by hydrophobic vitamin B_{12} derivatives, which are immobilized on electrodes.[22,23] It is shown in these studies that the hydrophobic vitamin B_{12} is clearly a promising catalyst for dehalogenation of chlorinated organic compounds.

Among the chlorinated organic compounds, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (**DDT**) is characterized by a pronounced insecticidal property and has been used worldwide for the last several decades despite its known hazardous effects on human health and wildlife. Because of recent environmental concerns, there is pressing need for efficient methods for degradation of such chlorinated compounds accumulated in the soil.[14–16] Therefore, much attention will be focused on the reaction between the hydrophobic vitamin B_{12} and **DDT** under electrochemical conditions. In this paper, electrolysis of **DDT** catalyzed by hydrophobic vitamin B_{12} was carried out as shown in Scheme 1.

Experimental

Materials

All solvents and chemicals used in the syntheses were of reagent grade, and were used without further purification. For electrochemical studies, dmf was stirred for one day in the presence of BaO under a nitrogen atmosphere, and distilled under reduced pressure. Deuterium solvents, dmf-d_7 (99.5% atom D) and deuterium oxide (D_2O) (99.9% atom D), were purchased from ACROS and CEA, respectively, and used without

† For Part 18 see ref. 22.

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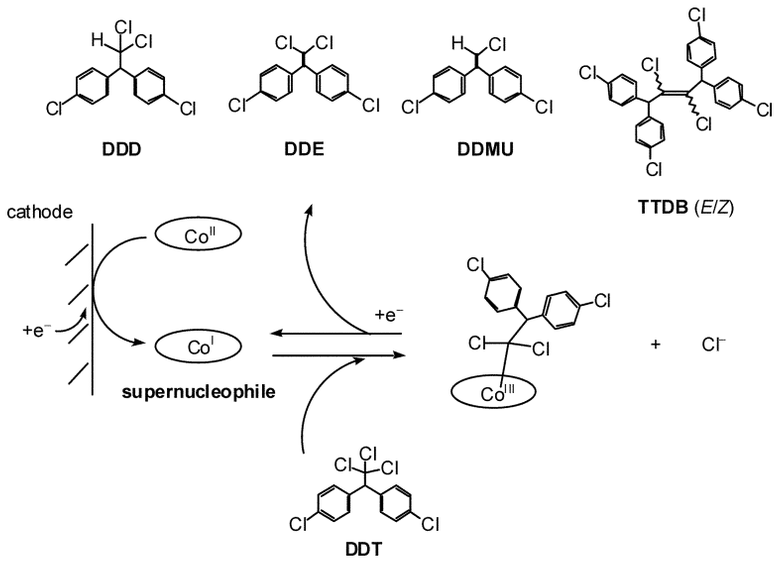


Scheme 1

further purification. 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, [Cob(II)7C_1ester]ClO_4, was synthesized by a previously reported method.[7,24] [Co(II)-(Hdmg)$_2$] (Hdmg = monoanion of dimethylglyoxime), was synthesized by the reported method.[25] 1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane, **DDT**, was purchased from Tokyo Kasei Kogyo (TCI) and was recrystallized from 2-propanol–water before use. α-Phenyl *N*-(*tert*-butyl)nitrone (PBN) was purchased from Aldrich and was used without further purification. TLC was performed on Merck Kieselgel 60 F254 precoated plates. Silica gel used for column chromatography was Silica Gel 60N (spherical: 60–210 μm, neutral) purchased from Kanto Chemical Co., Inc.

General analyses and measurements

Elemental analyses were obtained from the Service Center of Elementary Analysis of Organic Compounds at Kyushu University. The ^{1}H, ^{13}C, COSY, HMQC and HMBC NMR spectra were recorded on a Bruker Avance 500 spectrometer installed at the Center of Advanced Instrumental Analysis in Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. HPLC analyses were performed on a column of Inertsil ODS-3 (GL Scinences Inc.; length 150 mm; ID 4.6 mm, particle size 5 μm): flow rate, 1 mL min^{-1} (CH_3CN–H_2O) by employing an apparatus assembled with a Hitachi L-6200 intelligent pump, L-3000 photodiode array detector and D-2500 chromato-integrator. The GC-mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a column J&W Scientific DB-1 (length 30 m; ID 0.25 mm, film 0.25 μm). Gel permeation chromatography was carried out on a Japan Analytical Industry Co. Ltd., LC-908 apparatus combined with UV-3702 attachment, using three connected columns, JAIGEL-1H, 2H and 2.5H, with $CHCl_3$ eluent. The EPR spectra were obtained on a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter. The UV-VIS absorption spectra were measured on a Hitachi U-3300 spectrophotometer at room temperature.

Cyclic voltammetry

The cyclic voltammograms (CV) were obtained using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with a 1.6-mm diameter platinum wire as the working and counter electrodes were used. An Ag–AgCl (3.0 M NaCl) electrode served as a reference. Non-aqueous dmf solutions containing a cobalt complex (1.0×10^{-3} M) and *n*-Bu_4NClO_4 (1.0×10^{-1} M) were deaerated prior to each measurement, and the inside of the cell was maintained under an argon atmosphere throughout each measurement. All measurements were carried out at room temperature. The $E_{1/2}$ value of ferrocene–ferrocenium (Fc/Fc^+) was 0.56 V *vs.* Ag–AgCl with this setup.

Electrolysis of DDT

The controlled-potential electrolysis of **DDT** was carried out at −1.40 V *vs.* Ag–AgCl in the presence of [Cob(II)7C_1ester]ClO_4 in a cylindrical three-electrode cell which was divided into two internal compartments with a single sheet of microporous polypropylene membrane equipped with a platinum mesh cathode and a zinc plate anode (1×3 cm^2) at 308 K under an argon atmosphere. The applied potential between the working and reference electrodes during the electrolysis was maintained constant with a Hokuto Denko HA-501 potentiostat/galvanostat, and the reaction was monitored on a Hokuto Denko HF-201 coulomb/ampere-hour meter. Initial concentrations: cobalt complex, 5.0×10^{-4} M; **DDT**, 5.0×10^{-2} M; dmf solution containing 0.1 M *n*-Bu_4NClO_4. After the electrolysis, dmf was removed by evaporation under reduced pressure and 30 mL of $CHCl_3$ was added to the residue. The chloroform layer was washed with water (3×40 mL) to remove dmf completely, and dried with $MgSO_4$. Then the filtrate was concentrated to dryness. The residue was passed through a silica gel short column eluting with $CHCl_3$ to remove *n*-Bu_4NClO_4 and hydrophobic vitamin B_{12}, and then the products were analyzed by HPLC, NMR and GC-MS.

Isolation and identification of products

The products were separated by gel permeation chromatography and preparative TLC after the above work-up procedure, and characterized as follows. The products, 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (**DDD**) and 1,1-bis(4-chlorophenyl)-2,2-dichloroethylene (**DDE**) were identified by HPLC and GC-MS comparison with authentic samples which were purchased from TCI, and 1-chloro-2,2-bis(4-chlorophenyl)ethylene (**DDMU**) was identified by ^{1}H, ^{13}C NMR and GC-MS analyses.[26] The dimers, 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene (**TTDB** (*E*/*Z*)), were identified by ^{1}H, ^{13}C, HMQC and HMBC NMR and mass spectral comparison to the reported values.[27]

DDMU: mp. 65 °C, ^{1}H NMR ($CDCl_3$): δ 6.61 (s, 1H, CH), 7.15 (d, 2H, Ph), 7.30 (m, 4H, Ph), 7.41 (d, 2H, Ph), ^{13}C NMR: δ 116.8, 128.6, 128.8, 128.9, 131.2, 134.2, 134.4, 135.5, 138.2,

141.8. EI MS, *m/z*: $[M]^+$, 282. Found: C, 59.38; H, 3.23. Calc. for $C_{14}H_9Cl_3$: C, 59.30; H, 3.20%.

TTDB (*E*): R_f = 0.82 (eluent, *n*-hexane–$CHCl_3$ = 10 : 1), mp 234 °C, ^{1}H NMR ($CDCl_3$): δ 5.95 (s, 2H, methine), 7.09 (d, 8H, Ph), 7.29 (d, 8H, Ph), ^{13}C NMR: δ 52.7, 128.8, 130.3, 133.0, 133.4, 137.7. EI MS, *m/z*: $[M]^+$, 564. Found: C, 59.46; H, 3.21. Calc. for $C_{28}H_{18}Cl_6$: C, 59.30; H, 3.20%.

TTDB (*Z*): R_f = 0.74 (eluent, *n*-hexane–$CHCl_3$ = 10 : 1), mp 171 °C, ^{1}H NMR ($CDCl_3$): δ 5.55 (s, 2H, methine), 7.00 (d, 8H, Ph), 7.28 (d, 8H, Ph), ^{13}C NMR: δ 52.8, 128.8, 130.4, 133.7, 134.3, 137.7. EI MS, *m/z*: $[M]^+$, 564. Found: C, 59.36; H, 3.31. Calc. for $C_{28}H_{18}Cl_6$: C, 59.30; H, 3.20%.

Results and discussion

Redox behavior of hydrophobic vitamin B_{12} in the presence of DDT

A redox potential for the Co(II)/Co(I) couple of hydrophobic vitamin B_{12} in dmf was observed at −0.49 V *vs.* Ag–AgCl (−1.05 V *vs.* Fc/Fc^+) as shown in Fig. 1(a). The hydrophobic vitamin B_{12} is easily reduced to a supernucleophilic Co(I) species. The addition of an excess of **DDT** dramatically changed the voltammetric pattern and gave rise to a new irreversible redox wave at *ca.* −1.4 V *vs.* Ag–AgCl as shown in Fig. 1(b), which is ascribed to the reduction of an organocobalt complex formed in the electrolysis process.[28] This voltammetric pattern is in agreement with that for heptamethyl methylaquacobyrinate perchlorate in dmf.[8] To the extent that such a result involved an alkylated-cobalt species formed *in situ*, it was expected that the desired dechlorination process for **DDT** could take place. Based on this result, a preparative electrolysis

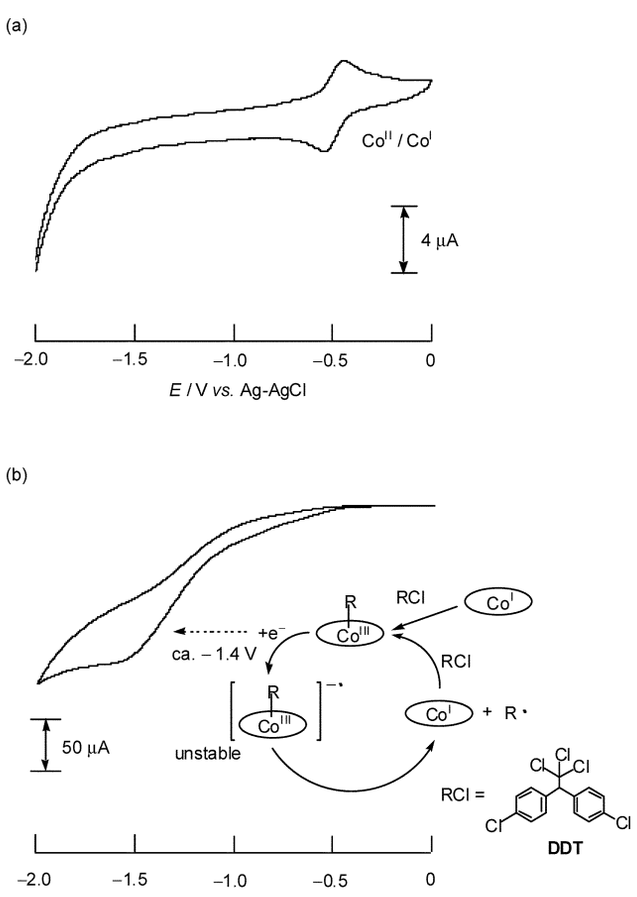


Fig. 1 Cyclic voltammograms of hydrophobic vitamin B_{12} in dmf containing 1.0×10^{-1} M *n*-Bu_4NClO_4 at room temperature; sweep rate: 100 mV s^{-1}: (a) 1.0×10^{-3} M [Cob(II)7C_1ester]ClO_4 and (b) 1.0×10^{-3} M [Cob(II)7C_1ester]ClO_4 and 1.0×10^{-2} M **DDT**.

reaction of **DDT** was performed in the presence of a catalytic amount of hydrophobic vitamin B_{12} as described below.

Controlled-potential electrolysis of DDT

The electrolyses were carried out at −1.4 V *vs.* Ag–AgCl in a cylindrical three-electrode cell which was divided into two internal compartments with a single sheet of microporous polypropylene membrane equipped with a platinum mesh cathode and a zinc plate anode. After a charge of 1.4 electron/molecule based on the substrate was passed, almost no electrolysis current was detected. Then, the products were analyzed by the procedure described in the Experimental section. **DDT** was decomposed by over 80% based on its initial concentration, and the turnover number based on the hydrophobic vitamin B_{12} as a catalyst was *ca.* 80. The dechlorinated products, **DDD**, **DDE**, **DDMU** and dimers **TTDB** (*E*/*Z*) were detected by HPLC and GC-MS analysis as shown by entry 1 in Table 1. Reductive dechlorination of **DDT** did not proceed under the corresponding conditions without hydrophobic vitamin B_{12} as a catalyst as shown by entry 2 in Table 1. In addition, it should be noted that the catalyst was recovered quantitatively after the electrolysis based on electronic and mass spectrometric analysis. In contrast, the electrolyzed solution of [Co(II)(Hdmg)$_2$], which is a well-known functional model compound of cobalamin, was decolorized under the same conditions during the course of the electrolysis and a small amount of **DDT** was dechlorinated as shown by entry 3 in Table 1. Therefore, the hydrophobic vitamin B_{12} is a tough and excellent catalyst.

Mechanistic aspects of the catalytic process

The controlled potential electrolysis was followed by electronic spectroscopy. When the electrolysis was carried out at −1.40 V *vs.* Ag–AgCl, [Cob(II)7C_1ester]ClO_4 was transformed into the corresponding photo-sensitive complex with absorption maxima at 313, 354 and 470 nm (Fig. 2, spectrum A). Spectrum B in Fig. 2 was obtained by irradiation with visible light under aerobic conditions. These absorption maxima and the photochemical behavior are characteristic of those for the complex with a cobalt–carbon bond.[4] This result indicates that the electrolysis reaction proceeds *via* formation of an alkylated complex with the cobalt–carbon bond as an intermediate.

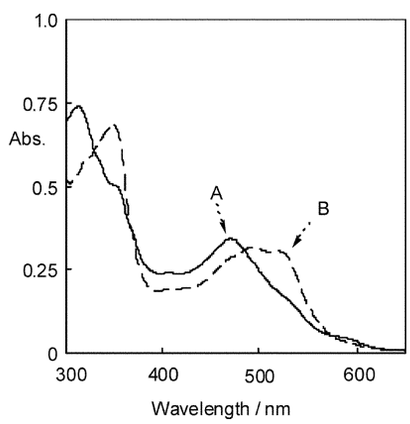


Fig. 2 Electronic spectra observed during electrolysis of a dmf solution containing [Cob(II)7C_1ester]ClO_4 (5.0×10^{-4} M), **DDT** (5.0×10^{-2} M) and *n*-Bu_4NClO_4 (1.0×10^{-1} M): A, at −1.4 V *vs.* Ag–AgCl; B, after irradiation with visible light under aerobic conditions.

The reaction mechanism was also examined by the spin-trapping technique with PBN.[29,30] An EPR spectrum was observed for the PBN spin adduct formed during the electrolysis at −1.40 V *vs.* Ag–AgCl: g = 2.007, A_N = 14.5 G, A_H = 3.7 G (10^4 G = 1 Tesla). Upon addition of PBN, the formation of the products was somewhat inhibited as shown by entry 4 in

Table 1 Electrolyses of **DDT** catalyzed by cobalt complexes[a]

Entry	Catalyst	Electrolyses conditions		Conversion[c] (%)	Product yields[d] (%)					
		Charge[b]/F mol^{-1}	Time/h		**DDD**	**DDE**	**DDMU**	(*E*)-**TTDB**	(*Z*)-**TTDB**	TN[e]
1	[Cob(II)7C$_1$ester]ClO$_4$	1.4	4	82	20	19	6	25	12	82
2	None	0.01	1	4	–	3	–	–	–	–
3	[Co(II)(Hdmg)$_2$]	0.08	1	9	3	4	–	–	–	7
4	[Cob(II)7C$_1$ester]ClO$_4$[f]	0.7	1	77	9	16	4	10	4	43
5	[Cob(II)7C$_1$ester]ClO$_4$[g]	1.4	3	91	17	11	9	18	6	61
6	[Cob(II)7C$_1$ester]ClO$_4$[h]	1.6	3	91	22	17	3	11	3	56

[a] Controlled-potential electrolyses were carried out in dmf at −1.40 V *vs.* Ag–AgCl under Ar atmosphere. Initial concentration: [catalyst], 5.0×10^{-4} M; **DDT**, 5.0×10^{-2} M; *n*-Bu$_4$NClO$_4$, 0.1 M. [b] Electrical charge passed per mol of **DDT**. [c] Conversion was estimated by the recovery of **DDT**. [d] Products were analyzed by NMR, HPLC and GC-MS. [e] Total turnover number (TN) based on the initial amount of the catalyst. [f] In the presence of PBN, 5.0×10^{-1} M. [g] Solvent, dmf-d$_7$. [h] In the presence of 5% D$_2$O. Yield of **DDD** is the sum of **DDD**-d$_1$ and **DDD** (see Chart 2)

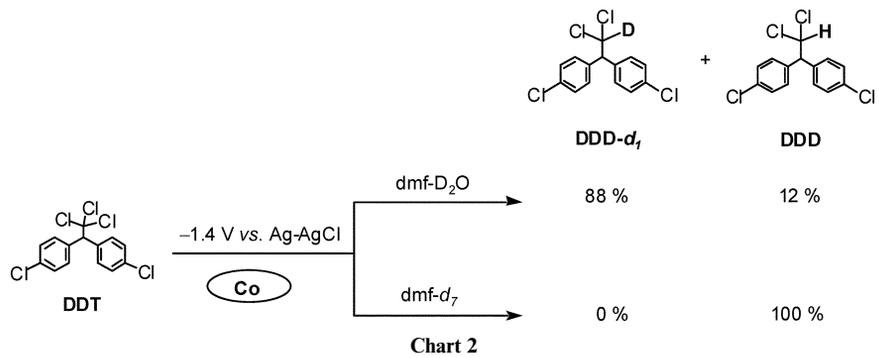
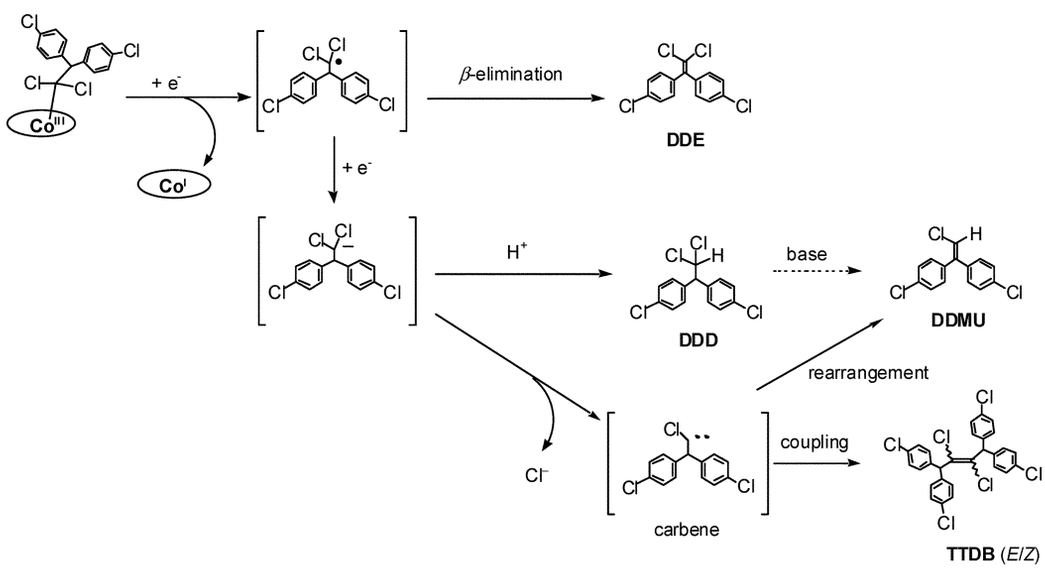


Chart 2



Scheme 2

Table 1. These results indicate that a radical species is generated as the electrolysis intermediate under the present conditions.

In order to determine the source of the hydrogen in the products, the electrolyses were carried out in dmf-d$_7$ and in dmf containing 5% D$_2$O. The distributions of products were analyzed by ^{1}H NMR and GC-MS, and the results are summarized in entries 5 and 6 in Table 1. The incorporation of deuterium did not occur in the reaction in dmf-d$_7$. In contrast, 88% of the deuterium ion was incorporated into **DDD** in the presence of D$_2$O as shown in Chart 2. Therefore, **DDD** was mainly produced from an anionic intermediate and not directly from a radical intermediate.

The proposed reaction mechanism is shown in Scheme 2. The Co(II) complex is electrochemically reduced to the Co(I) species, and the corresponding alkylated complex is generated by the reaction of the supernucleophilic Co(I) species with **DDT**. The alkylated complex is subsequently reduced by electrolysis at this potential to form the substrate radical and Co(I) species, and the cobalt complex acts as a mediator. **DDE** would be formed by β-elimination of the substrate radical and not by the disproportionation of the corresponding radical species. If disproportionation of the substrate radical occurred, a deuterium ion from D$_2$O would not be incorporated into **DDD**. (see Chart 2) At this electrolysis potential, further one-electron reduction of the substrate radical produces a carbanion and a subsequent protonation gives **DDD** as shown in Scheme 2. This carbanion may lead to a carbene with the elimination of the chloride ion,[31,32] and the carbene dimerises to **TTDB**. The minor product **DDMU** may be formed by a rearrangement of the carbene or by an elimination of HCl from **DDD**.

In conclusion, controlled potential electrolyses of **DDT** were carried out in dmf in the presence of a catalytic amount of hydrophobic vitamin B$_{12}$ to form various dechlorinated compounds. The environmental pollutant **DDT** was dechlorinated *via* formation of a cobalt–carbon bond under electrochemical conditions. The hydrophobic vitamin B$_{12}$ is one of the best

catalysts acting as an electrolysis mediator in the present system.

Acknowledgements

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