Enhanced reactivity of hydrophobic vitamin B_{12} towards the dechlorination of DDT in ionic liquid

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The electrolytic reductive dechlorination of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) in the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) in the presence of a cobalamin derivative afforded 1,1′-(ethylidene)bis(4-chlorobenzene) (DDO) and 1,1′-(ethenylidene)bis(4-chlorobenzene) (DDNU) with 1,1′-(2-chloroethylidene)bis(4-chlorobenzene) (DDMS); the enhanced reactivity, as well as the recyclability of the cobalamin derivative catalyst in IL, makes the present system more efficient for the development of "green" technologies.

Vitamin B_{12} derivatives are considered as some of the most effective catalysts for the dehalogenation of halogenated compounds,[1–3] which proceeds through the formation of Co(III)–alkyl intermediates.[3] Recently, a successful outcome for the dechlorination of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) in DMF mediated by heptamethyl cobyrinate perchlorate,[4] hydrophobic vitamin B_{12} [Co(II)] (Chart 1) was reported, where various dechlorinated products, mainly the mono-dechlorinated DDT-metabolites such as 1,1′-(2,2-dichloroethylidene)bis(4-chlorobenzene) (DDD) and 1,1′-(2,2-dichloroethenylidene)bis(4-chlorobenzene) (DDE), were produced.[3]

It is well-known that DDT is one of the most problematic POPs (persistent organic pollutants) and is found to cause serious health and developmental problems in human and wildlife even at low concentrations.[5] To date, the processes available for DDT dechlorination are either time-consuming or generate waste-containing solvents and catalysts. Herein, we will disclose a more effective and eco-friendly technique for the dechlorination of DDT and DDD in the ionic liquid (IL) [bmim][BF_4] (Chart 1). Utilizing the concept illustrated in Scheme 1, the aliphatic chlorines from the terminal carbon atom of the DDT moiety can be completely dechlorinated. Besides, we have utilized the advantages of IL as a reaction medium, avoiding the commonly used supporting electrolytes, which often create difficulties for its recovery. Moreover, ILs are often referred to as green solvents, showing low melting points, high polarity, negligible vapour pressure, non-flammability and good solubility for many organic and inorganic compounds.[6]

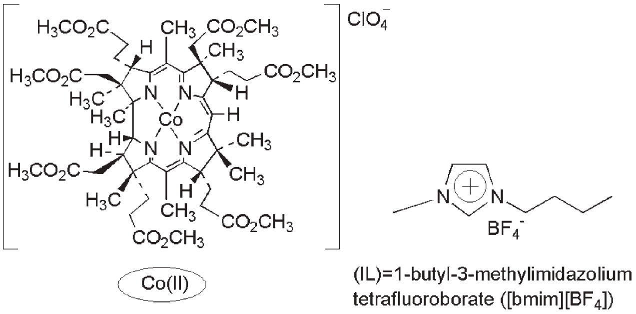
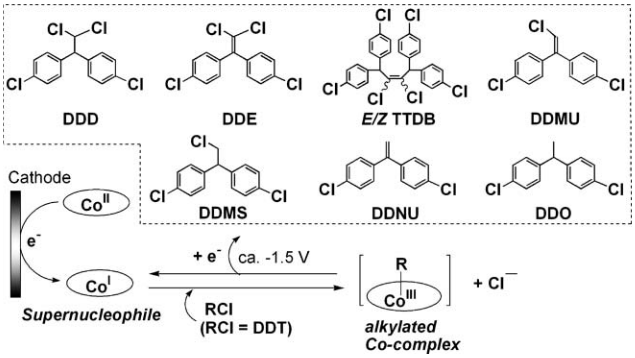


Chart 1 Co(II) and the IL used in this study.



Scheme 1 Co(II) mediated DDT dechlorination in IL.

Cyclic voltammetry (CV) of DDT in the presence of Co(II) in IL shows a broad cathodic peak (curve (i) in Fig. 1) at −1.35 V *vs.* Ag/AgCl with a huge amount of catalytic current for the reduction of the corresponding alkylated complex.

Based on this result, a series of bulk electrolyses of DDT were carried out at −1.5 V *vs.* Ag/AgCl using a cylindrical electrochemical cell consisting of a carbon felt working cathode, a sacrificial Zn-plate anode and an Ag/AgCl reference electrode in IL containing a catalytic amount of Co(II)†, and the results of which are shown in Table 1. Entries 1 and 4 of Table 1 show that the di- and tri-dechlorinated products were produced by the

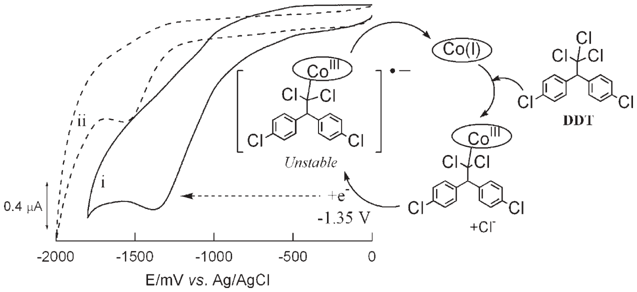


Fig. 1 CVs of 20 mM DDT in the presence (i) and absence (ii) of 0.5 mM Co(II) in IL. Scan rate: 100 mV s^{-1}.

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Table 1 Bulk electrolyses data of DDT catalysed by Co(II)

Entry	Solvent and additive	Conversion of DDT (%)	Yield (%)[d]						
			DDD	DDE	TTDB (*E*/*Z*)	DDMU	DDMS	DDNU	DDO
1[a]	IL, Co(II)	75	20	15	5/2	2	7	5	15
2[a]	Only IL	46	19	Trace	Trace	7	16	—	—
3[a,b]	DMF, Co(II)	82	20	19	25/12	6	—	—	—
4[a,c]	IL, Co(II)	95	—	16	3/2	Trace	27	Trace	44

[a] At −1.5 V *vs.* Ag/AgCl; Ar atmosphere; initial concentrations: DDT 2.5 × 10^{-2} M; Co(II) 5.0 × 10^{-4} M; charge passed: 2.1 F mol^{-1} of DDT. [b] 0.1 M Bu_4NClO_4 was used as a supporting electrolyte. [c] Prolonged electrolysis; charge passed: 4.0 F mol^{-1} of DDT. [d] Products were analyzed using ^1H NMR, HPLC and GC-MS data.

elimination of Cl-atoms from the terminal aliphatic carbon atom in the Co(II)–IL system. On the other hand, in the Co(II)–DMF system, no such kind of products were produced, as shown in entry 3 of Table 1. Furthermore, prolonged electrolysis (by passing 4.0 F mol^{-1}) converts over 95% of DDT into its dechlorinated products, with tri-dechlorinated 1,1′-(ethylidene)bis(4-chlorobenzene) (DDO) as the major product (entry 4). In this case, no DDD was produced, suggesting that all of the DDD had been converted into 1,1′-(2-chloroethylidene)bis(4-chlorobenzene) (DDMS) and/or DDO.

The Co(II)–IL system was further utilized for the dechlorination of the relatively less reactive DDD, which yielded DDMS and DDO as the major products (Table 2). Under the same conditions in DMF, the dechlorination proceeded with only 16% conversion.

The DDT dechlorination reaction mediated by Co(II) proceeds *via* the formation of an alkylated complex, with a cobalt–carbon bond, as the intermediate, which was followed using UV-Vis spectroscopy during electrolysis. When the electrolysis was carried out at −1.5 V *vs.* Ag/AgCl, the charge neutral Co(I) species converted to the corresponding photo-active complex with absorption maxima at 356 and 470 nm, respectively; absorption maxima at 410 and 505 nm, respectively, were recorded by irradiation of the same solution with visible light under aerobic condition. This photochemical behaviour is characteristic of that for a complex with a cobalt–carbon bond.[7]

The enhanced reactivity of the Co(II)–IL system over the Co(II)–DMF system could be explained by the application of the Hughes–Ingold predictions[8] of solvent polarity effects on reaction rates. The E_T scale is one of the most widely applied of empirical polarity scales.[9] For [bmim][BF_4] and DMF, the $E_T(30)$-values are 52.5 and 43.2 kcal mol^{-1}, respectively,[10] indicating the comparatively more polar behaviour of IL. The reaction of electrochemically generated Co(I) with DDT is a "Menschutkin type of reaction" in which two neutral reactants, Co(I) and DDT, react to form charged products *via* a charge-separated activated complex in the polar IL, which ultimately decreases the $\Delta G^{\ddagger}$ value, resulting in an increase in the reaction rate.

Table 2 Bulk electrolyses data of DDD catalysed by Co(II)

Entry	Solvent and additive	Conversion of DDD (%)	Yield (%)[c]		
			DDMS	DDNU	DDO
1[a]	IL, Co(II)	77	61	Trace	13
2[a]	Only IL	Trace	—	—	—
3[a,b]	DMF, Co(II)	16	10	—	Trace

[a] At −1.5 V *vs.* Ag/AgCl; Ar atmosphere; initial concentrations: DDD 2.5 × 10^{-2} M; Co(II) 5.0 × 10^{-4} M; charge passed: 2.2 F mol^{-1} of DDD. [b] 0.1 M Bu_4NClO_4 was used as a supporting electrolyte. [c] Products were analyzed using ^1H NMR, HPLC and GC-MS data.

The Co(II) has been recycled and reused for the dechlorination of DDT in IL, where the conversions of DDT to its dechlorinated products were found to be in the range of 73–82%. After the fourth run, over 96% recovery of Co(II) was obtained without its decomposition, as examined using UV-Vis spectroscopy and MALDI-TOF mass spectrometry. Thus, Co(II) is proved to be a tough catalyst for the dechlorination of DDT.

The present study successfully demonstrates the electrolytic dechlorination of DDT and DDD in a Co(II)–IL system. The use of the cheaper material, carbon felt, for the cathode and the recyclability of the Co(II) in IL system makes the process cost-effective and eco-friendly.

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Notes and references

† After the electrolysis, the catholyte was extracted with diethyl ether (3 × 10 mL). The diethyl ether portion contains the mixture of dechlorinated products. The other portion, containing IL and Co(II), was further dried in vacuum and recycled for the next run.

DDD and DDE were identified using GC-MS and HPLC comparison to authentic samples. DDMU 1,1′-(2-chloroethenylidene)bis(4-chlorobenzene) and TTDB (*Z*/*E*) 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene were identified from spectral comparison to the reported values.[11,12] DDMS was obtained as a pale yellowish solid; GC-MS: *m*/*z*: 284 [M^+]; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.0 (d, 2 H), 4.30 (t, 1 H), 7.3 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$): 46.64, 52.28, 128.95, 129.32, 133.16, 139.29 ppm. DDO was obtained as a colorless mass; GC-MS: *m*/*z*: 250 [M^+]; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.6 (d, 3 H), 4.1 (q, 1 H), 7.3 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$): 22.14, 44.02, 129.00, 129.31, 129.75, 131.73 ppm. DDNU was obtained as colorless solid crystals;[13] mp 83 °C; GC-MS: *m*/*z*: 248 [M^+]; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.48 (s, 2 H), 7.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$): 115.5, 128.9, 129.9, 134.3, 139.9, 148.3 ppm.

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