



Highly efficient C–Cl bond cleavage and unprecedented C–C bond cleavage of environmentally toxic DDT through molecular electrochemical catalysis

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ABSTRACT

The electrocatalytic properties of a Co(II)octaalkoxyphthalocyanine complex (Co(II)Pc) with eight strongly electron-donating substituents provide the first example of the complete dechlorination of DDT through molecular electrocatalysis, rather than the use of metal electrodes which had been achieved previously. Interaction with a highly nucleophilic $[\text{Co}(\text{I})\text{Pc}]^{2-}$ species results in rapid cleavage of the $\text{C}_{(\text{sp})^3}\text{--Cl}$, $\text{C}_{(\text{sp})^2}\text{--Cl}$ and aromatic $\text{C}_{(\text{sp})^2}\text{--Cl}$ bonds. Bis(*p*-chlorophenyl)methanone (BPCL₂) is detected in high yield along with its full dechlorination product, diphenylmethanone (BP) and the conventional C–Cl bond cleavage products, due to an unprecedented C–C bond cleavage reaction that is followed by the formation of a C–O bond. Theoretical calculations are used to analyze trends in the electronic structure of the Co(II)octaalkoxyphthalocyanine complex that account for the efficiency of the C–Cl bond cleavage reactions, and the reaction process and mechanism are analyzed in depth.

1. Introduction

Over the past few decades, organochlorides, organic compounds with at least one covalent C–Cl bond, such as 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), pentachlorophenol (PCP), polychlorinated biphenyls (PCBs) and hexachlorocyclohexane (PCCH) have been used in a wide range of applications [1–4]. Unfortunately, organochlorides often do not degrade in the environment, so despite restrictions being placed on their use in agriculture in many countries, they are still present around the world at significant concentrations as a ubiquitous contaminant in soils and waters [5–8]. There has been considerable interest in the development of new techniques to achieve their full degradation through C–Cl bond cleavage reactions. This has included microbial methods [9–14], along with chemical [15–19], photochemical [20–25] and electrochemical approaches [26–31].

There has been considerable interest in electrocatalytic processes due to their facile procedures and low cost. Electrocatalysis usually makes use of macrocyclic transition metal complexes, such as phthalocyanines (Pcs), porphyrins and cycloamines [32,33]. Typically, when a phthalocyanine is used, a central divalent metal ion is reduced electrochemically to form a $[\text{M}^{\text{I}}\text{Pc}(-2)]^{-}$ species, so it can react with alkyl halides (R–X) to form a σ -bond and a M^{III} -macrocycle, since this results

in the release of a chloride ion through the cleavage of a C–Cl bond [34,35]. The dissociation energy of the bond is determined by the type of s-p hybridization that is involved. The values for $\text{C}_{(\text{sp})^3}\text{--Cl}$ bonds lie in the 330–350 kJ/mol range, whereas those of $\text{C}_{(\text{sp})^2}\text{--Cl}$ and aromatic $\text{C}_{(\text{sp})^2}\text{--Cl}$ bonds lie in the 370–390 kJ/mol range and close to 400 kJ/mol, respectively [36–42]. The efficiency of C–Cl bond cleavage reactions differs significantly, therefore. For example, when iron(III)porphyrins were used as electroreductive catalysts for the dechlorination of lindane, pentachlorocyclohexene (PCCH), tetrachlorocyclohexadienes (TCDNs) and trichlorobenzenes (TCBs) were formed through the activation of the $\text{C}_{(\text{sp})^3}\text{--Cl}$ bond, but there was no significant degradation of the more stable aromatic $\text{C}_{(\text{sp})^2}\text{--Cl}$ bonds of the trichlorobenzenes [22,24].

One main challenge for researchers active in the field of electrocatalysis is to develop catalysts that can enable the complete dechlorination of environmentally problematic organochlorides, such as DDT. When Co^{II} , Fe^{III} and Mn^{III} porphyrins and Co^{II} phthalocyanines have previously been used as electrocatalysts, DDT has been degraded to form 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD), (1,1-bis(4-chlorophenyl)-2,2-dichloroethylene) (DDE), and (1,1-bis(4-chlorophenyl)-2-chloroethylene) (DDMU) since full $\text{C}_{(\text{sp})^3}\text{--Cl}$ bond cleavage occurs followed by partial cleavage of the $\text{C}_{(\text{sp})^2}\text{--Cl}$ bonds [20,21,23].

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