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A new bipyridyl cobalt complex for reductive dechlorination of pesticides

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ABSTRACT

Reductive dechlorinations are especially promising reactions for improving the biodegradability and hence decreasing the environmental impact of chlorinated organic pollutants. In this context, the catalytic activity of a bipyridyl cobalt complex containing two bipyridine ligands was examined for achieving clean electrochemical dehalogenation in aqueous media. The prepared $[Co(bpy(CH_2OH)_2)_2]^{2+}$ complex was found to exhibit high catalytic activity toward the dechlorination of chloroacetanilide herbicides. Based on preparative electrolyses, 2-electron reduction of the substrate was obtained with a dechlorination yield of 85%, underlining the selectivity and efficiency of the dehalogenation process. Cyclic voltammetry analyses highlighted the catalytic activity of the complex toward chloroacetanilide herbicides, as alachlor, metolachlor and metazachlor. An high apparent chemical rate constant k_1 of $5000\,mol^{-1}\,L\,s^{-1}$ is calculated for the first step of the cathodic reduction of alachlor, based on simulated cyclic voltammetry experiments.

1. Introduction

Chlorinated organic compounds are widely used in synthetic chemistry and are prominent environmental contaminants as many of them are biorecalcitrant. Several physico-chemical methods have been proposed for their degradation [1–6]. Among them, the catalytic reduction of chlorinated compounds has been the subject of numerous investigations because of its high importance both for synthetic chemistry and environment [6–11]. Transition metal complexes such as Co(I) complexes have been identified as effective catalysts for this reaction [12–15], the reactivity of the catalyst depending on the ligands structure. $[Co(salen)]^-$ (salen = bis(salicyliden)ethylenediamine) has shown good catalytic activity toward alkyl iodide, bromide and chloride such as *tert*-butyl bromide and chloride [16], *n*-butyl bromide and iodide, 1,2-dibromobutane [17,18], iodoethane [19], some of them containing a carbon in α position of a carbonyl (3-chloro-2,4-pentanedione) or a phenyl group ($PhCCl_3$ [14], benzal chloride [20,21], and benzyl chlorides [22]). Whereas $[Co(salen)]^-$ catalytic activity toward the reduction of bromobenzene has been reported once [23], it is not reported as a good catalyst for the reduction of aryl halides. Cobalt chelates of biological interest such as cobalt porphyrins, and cobalamin have shown good catalytic activity toward reduction of alkyl bromide and chlorine [24–26], ethylenes [27–29], and arenes [30–32]. Two different general mechanisms have been proposed for the catalysis depending on the ligand L, the halogenated compound and the electrolyte. These schemes differ by the nature of electron transfer step that involved the formation of the intermediate radical $R^{\cdot}$ (outer-sphere) or an oxidative addition (inner-sphere) (Scheme 1) [18,27,33–35].

Concerning the possible uses for an environmental purpose, some of these complexes have been reported to keep their catalytic activity in aqueous media, which is a requirement for such application [12,24,32,36]. Among the possible catalysts, polypyridyl complexes of cobalt are promising candidates as they display good catalytic activity for indirect electroreduction of allyl chloride in aqueous medium [15,37,38]. However, the number of bipyridyl units coordinated to the metal strongly affects the catalytic behavior of the Co(I) polypyridyl complexes, such effect depending on the medium, electrolyte, substrates, . . . It was previously established that the catalytic behavior of $Co(bpy)_3^{2+}$ toward the reduction of allyl chloride in acetonitrile involves the reduction of Co(II) to Co(I) followed by a rapid decomposition into $Co(bpy)_2^+$ (Scheme 2), the ligand dissociation step (Eq. 2) being the rate-

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$$[Co^{I}(L)]^- + RX \rightarrow [Co^{III}R(L)] + X^- \text{ (Inner-sphere)}$$

$$[Co^{I}(L)]^- + RX \rightarrow [Co^{II}(L)] + X^- + R^\cdot \text{ (Outer-sphere)}$$

Scheme 1. Inner-sphere and outer-sphere mechanisms of dehalogenation reactions catalyzed by Co^{I} complexes.

$$Co(bpy)_3^{2+} + e^- \rightleftharpoons Co(bpy)_3^{+} \qquad (1)$$

$$Co(bpy)_3^{+} \rightleftharpoons Co(bpy)_2^{+} + bpy \qquad (2)$$

Scheme 2. Cathodic reduction of Co(bpy)$_3^{2+}$ complex involving a loss of a bipyridyl ligand.

determining step and the Co(bpy)$_2^+$ being the active catalytic species [39,40].

This conclusion was supported by the observation of a higher catalytic efficiency with Co(bpy)$_2^+$ than with Co(bpy)$_3^+$. More recently, it was reported that CoBr$_2$ in the presence of a single equivalent of 2,2′-bipyridine or pyridine exhibits a high catalytic activity toward the reduction of aromatic halides [41,42]. In an aqueous solution containing a surfactant, the reduced tris-complex was stabilized in the micelle and a mild kinetic enhancement was reported in the catalytic reduction of allyl halides by the Co(bpy)$_3^+$ complex. However, the exact nature of the active catalyst remains difficult to establish as little is known about the activity of the corresponding Co(bpy)$_2^+$ complex in such aqueous conditions.

In this context, we have considered the catalytic activity toward dechlorination reaction of a new polypyridyl complex that contains only two bipyridyl units: [Co(bpy(CH$_2$OH)$_2$)$_2$]$^{2+}$ where bpy(CH$_2$OH)$_2$ is 4,4′-Bis (hydroxymethyl)-2,2′-bipyridine. In view of potential environmental applications, its catalytic behavior was investigated in aqueous medium by cyclic voltammetry toward the reduction of several different common chlorinated pesticides. In complement to the cyclic voltammetry investigations, bulk electrolysis were also performed to precise the dependence of the catalytic efficiency on the structure of the chlorinated compound. The considered pesticides: alachlor **1**, metazachlor **2**, metolachlor **3**, 2,4-D **4** and the dechlorinated form of alachlor **5**, are shown in Scheme 3.

2. Experimental

2.1. Chemicals

Alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide), metazachlor (2-chloro-*N*-(2,6-dimethylphenyl)-*N*-(1H-pyrazol-1-ylmethyl)acetamide), metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(1-methoxypropan-2-yl)acetamide), [2,2'-bipyridine]-4,4'-dicarboxylic acid, sodium borohydride and Cobalt(II) tetrafluoroborate hexahydrate were purchased from Sigma-Aldrich. 2,4-D (2-(2,4-dichlorophenoxy)acetic acid) and hexadecyl trimethyl ammonium bromide (HDTAB) were supplied by Alfa Aesar. Deschloroalachlor (*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) was obtained from Alpha Chimica (France). Graphite felt (Recycled Vein Graphite RVG 4000) was supplied by Mersen (France). Its specific area measured by the BET (Brunauer, Emett and Teller) method, its volume density and its carbon content were 0.7 m^2 g^{-1}, 0.088 g cm^{-3} and 99.9%, respectively.

2.2. Synthetic procedures

The following procedure for the preparation of [2,2'-bipyridine]-4,4'-diyldimethanol **8** was modified from literature conditions [43].

2.2.1. Synthesis of diethyl [2,2'-bipyridine]-4,4'-dicarboxylate *7*

[2,2'-bipyridine]-4,4'-dicarboxylic acid **6** (500 mg, 2 mmol) was added to absolute ethanol (40 mL). Concentrated sulfuric acid (95%) (0.5 mL) was added to the suspension and the mixture was refluxed for 4 days. The solution was cooled to room temperature, distilled water was added (40 mL) and ethanol was then evaporated. The pH was adjusted to 7 using a 5% sodium hydroxide solution. The formed precipitate was filtrated and washed with water, leading to a white powder. Yield; 92%, ^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 1,38 (t, 6H, J = 7 Hz); 4.40 (q, 4H, J = 7 Hz); 7.85 (d, 2H, J = 6 Hz); 8.80 (d, 2H, J = 6 Hz); 8.88 (s, 2H).

2.2.2. Synthesis of [2,2'-bipyridine]-4,4'-diyldimethanol *8*

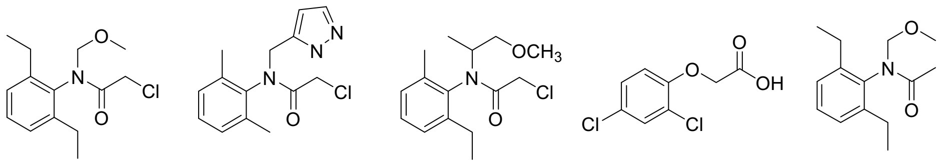
Sodium borohydride (1.87 g, 49 mmol) was added to a suspension of diethyl [2,2'-bipyridine]-4,4'-dicarboxylate **7** (567 mg, 1.89 mmol) dissolved in absolute ethanol (34 mL). The solution was refluxed for 3 h. After cooling to room temperature, a saturated ammonium chloride solution (24 mL/g of NH$_4$Cl) was added to decompose the excess of sodium borohydride. Ethanol was evaporated under vacuum and the resulting solid was dissolved in a minimum of water using ultrasonic bath. The solution was extracted with ethyl acetate (5 × 34 mL), dried on sodium sulfate and concentrated under vacuum to give a white powder. Yield: 91%, ^{1}H NMR (CD$_3$OD, 300 MHz): δ (ppm) 4.66 (s, 4H); 7.35 (d, 2H, J = 5 Hz); 8.18 (s, 2H); 8.50 (d, 2H, J = 5 Hz).

2.2.3. Synthesis of [Co(bpy(CH$_2$OH)$_2$)$_2$](BF$_4$)$_2$ *9*

Cobalt(II) tetrafluoroborate hexahydrate (156 mg, 0.46 mmol) was added to 4,4′-Bis(hydroxymethyl)-2,2′-bipyridine **8** (408 mg, 1.89 mmol) dissolved in absolute ethanol (37 mL). The solution was refluxed under stirring for 24 h, concentrated and dried under vacuum. The solid was dissolved in a minimum of methanol and dichloromethane was added slowly. The formed precipitate was filtrated and washed with dichloromethane, leading to a yellow solid. Yield: 95%, HRMS (ESI): *m/z* calcd for $C_{24}H_{24}N_4O_4Co$ [M-2BF$_4$]$^{++}$: 245.5559; found, m/z 245.5559; Found, C, 43.68; H, 4.06; N, 8.27Calc. for $C_{24}H_{24}BrCoF_8N_4O_4$: C, 43.35; H, 3.64; N, 8.42%.

2.3. Dechlorination conditions

The dechlorination reaction was performed in a home-made flow cell [44]. To ensure a good homogeneity of the potential distribution in the three dimensional working electrode, the felt



Alachlor **1** Metazachlor **2** Metolachlor **3** 2,4-D **4** Deschloroalachlor **5**

Scheme 3. Structure of the pesticides involved in this study and of deschloroalachlor.