

FOOT-OF-THE-WAVE ANALYSIS OF THE ELECTROCATALYTIC DECHLORINATION OF HEXACHLOROETHANE USING COBALOXIMES

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ABSTRACT

In this work the electrochemical degradation of polychlorinated compounds using Co(dmgH)₂Cl(py), Co(dpgH)₂Cl(py), Co(chgH)₂Cl(py) and Co(dbegH)₂Cl(py) (where dmgH is dimethylglyoximate, dpgH is diphenylglyoximate, chgH is 1,2-cyclohexanedionedioximate and dbegH is 4,4'-((1E,2E)-1,2-bis(hydroxyimino)ethane-1,2-diyl)dibenzoate) is described. The degradation was studied using cyclic voltammetry by monitoring current changes in the zone near to the Co(II/I) half wave potential as the concentration of the organochloride in the electrochemical cell is increased. Hexachloroethane (HCA) was used as organohalide substrate, while gamma-hexachlorocyclohexane (lindane), 1,2-dichloroethane, and 1,1,1-trichloroethane were used for comparative studies. The major dechlorination product of HCA, detected through head space GC-MS experiments after bulk electrolysis, was tetrachlorethylene. The rate constants of the dechlorination processes were estimated using the *foot-of-the-wave* analysis (FOWA), the values obtained were 1.10×10⁵, 2.59×10⁴, 4.91×10⁴ and 1.83×10⁴ for Co(dmgH)₂Cl(py), Co(dpgH)₂Cl(py), Co(chgH)₂Cl(py) and Co(dpegH)₂Cl(py) respectively.

Keywords: Cobaloxime; cyclic voltammetry; organochlorines; catalysis.

1. INTRODUCTION

The compounds that have multiple chlorine atoms in their structure could be dangerous for human health^{1,2}. Prolonged exposure to these type of compounds can generate various problems such as central nervous system disorders³, cardiovascular diseases⁴, depression of the immune system⁵ or cancer⁶⁻⁸.

They also could be harmful for the environment, and despite the restrictions that are applied for their use, they are widely employed in agriculture as pesticides or herbicides, becoming ubiquitous pollutants in soils and waters⁹.

The cleavage of the C-Cl bonds could lead to safer products, e.g. vinyl chloride, a known carcinogen, produces non-toxic ethylene after their dechlorination^{10,11}. In this context, different strategies have been explored to cleavage carbon-chlorine bonds such as biodegradation¹², the use of zero valent iron¹³ and the catalytic reduction with molecular catalysts¹⁴⁻¹⁶. The latter is the most interesting because the catalysts can be tailored by introducing structural modifications in order to improve the catalytic activity in the degradation of specific pollutants.

Cobaloximes¹⁷ are a class of molecular catalysts based on cobalt and glyoxime ligands which are capable to participate in reductive dechlorination reactions since they are strong nucleophiles upon reaching the Co(I) state. The electrochemical reduction potential of the Co(II/I) couple can be tuned by making structural modifications to the glyoxime ligands, generally introducing electron withdrawal groups on the ligands will displace the Co(II/I) potentials towards more positive values. In literature it has been reported that these changes could result in a decrease of the activity for some catalytic processes¹⁸⁻²², nevertheless we have recently reported the use of cobaloximes for the catalytic reduction of hexachloroethane to tetrachloroethene employing a series of cobaloximes where the Co(II/I) reduction potential was tuned in the -0.91 to -0.69 V vs Ag/AgCl range by varying the substituents on the glyoxime ligand, and found little differences in observed rate constant using the total catalysis model²³.

This model could not be the best to describe the kinetics of these systems, therefore in this work we will use the *foot-of-the-wave* (FOWA) model to analyze the electrochemical behavior of a family of cobaloxime complexes as catalysts in the dechlorination of several organochlorine compounds.

2. EXPERIMENTAL

3.1. Materials and measurements

All the chemicals were commercially available and used as received. Co(dmgH)₂Cl(py)²⁴, Co(dpgH)₂Cl(py)²⁵, Co(chgH)₂Cl(py)²⁶ and Co(dbegH)₂Cl(py)²⁷ were synthesized according to procedures reported in literature. The organochlorine compounds employed for the catalytic

degradation experiments were HCA, 1,2-dichloroethane and 1,1,1-trichloroethane.

2.2. Electrochemistry

Cyclic voltammetry experiments were conducted on a Princeton Applied Research PG 580 potentiostat/galvanostat using a three-electrode single compartment cell including a glassy carbon working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode. Tetrabutylammonium hexafluorophosphate [NBu₄][PF₆] was used as the supporting electrolyte (0.1 mol L⁻¹). For all measurements, samples were degassed by purging with nitrogen.

Cyclic voltammograms were acquired using a 0.1 mmol L⁻¹ solution in cobaloxime and adding small aliquots of the organochlorine compounds in order to increase their concentration from 0.1 to 14 mmol L⁻¹.

2.3. Bulk electrolysis experiments

A homemade electrolysis cell suited with a carbon mesh as the working electrode, platinum wire as the auxiliary electrode and an Ag/AgCl reference electrode was used. In a typical experiment 10 mL an acetonitrile 0.1 M [NBu₄][PF₆] solution containing 1.4 mmol L⁻¹ of the catalyst and 14 mmol L⁻¹ of the organochlorine was purged with N₂, then was subjected to electrolysis for a period of 60 minutes at -0.95 V.

2.4. Headspace experiments

Headspace combined with gas chromatography-mass spectrometry (GC-MS) was used to analyze the volatile organic compounds (VOCs) after the bulk electrolysis experiments. The sample vials containing 200 μL of the post-reaction solution were oven heated for 20 min at 100 °C, then 5 μL of the headspace were injected into the port of an Agilent Technologies GC-MS 5890A with a HP-5ms column (30m x 0.25mm x 0.25 μm). The injection port was in a split mode (1:10) with a Helium flow of 1.0 mL min⁻¹. The initial oven temperature was 80 °C ramped at 10 °C min⁻¹ to 200 °C. The temperature of MS Quad 120 °C and 230 for the MS Source. The scan parameters were 50 to 300 m/z.

3. RESULTS AND DISCUSSION

The structures of all the complexes used in this study are presented in Fig. 1. The cyclic voltammograms of these compounds are shown in Fig. S1 in the supporting information. They show an irreversible process assigned to the reduction of the pair Co (III)/Co(II) and a reversible reduction process assigned to the reduction of the pair Co (II)/Co(I), the reduction potential values are presented in table 1, this behavior is consistent with the reported in the literature²⁸.

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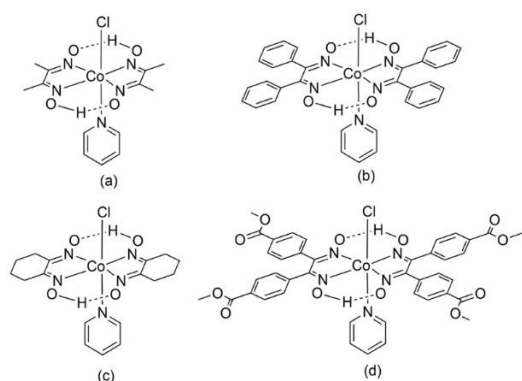


Figure 1. Structures of the cobaloximes used in this study: (a) $\text{Co}(\text{dmgH})_2\text{Cl}(\text{py})$; (b) $\text{Co}(\text{dpgH})_2\text{Cl}(\text{py})$; (c) $\text{Co}(\text{chgH})_2\text{Cl}(\text{py})$ and (d) $\text{Co}(\text{dbegH})_2\text{Cl}(\text{py})$.

In cyclic voltammetry experiments, the addition of HCA to a cobaloxime solution led to the appearance of a considerable current increase in the zone near the $\text{Co}(\text{II/I})$. This behavior is exemplified in Fig. 2a which shows the change in the cyclic voltammograms of $[\text{Co}(\text{dbegH})_2\text{Cl}(\text{py})]$ in DMF 0.1 mol L^{-1} $[\text{NBu}_4][\text{PF}_6]$ at a scan rate of 100 mVs^{-1} after the addition of 0.3 - 1.4 mmol L^{-1} of HCA. The electrochemical response of $\text{Co}(\text{dmgH})_2\text{Cl}(\text{py})$, $\text{Co}(\text{dpgH})_2\text{Cl}(\text{py})$ and $\text{Co}(\text{chgH})_2\text{Cl}(\text{py})$ versus HCA are shown in Fig. S2, S3 and S4 in the supporting information. These changes in the electrochemical response are indicative of the catalytic activity of the complex in the dechlorination of the substrate.

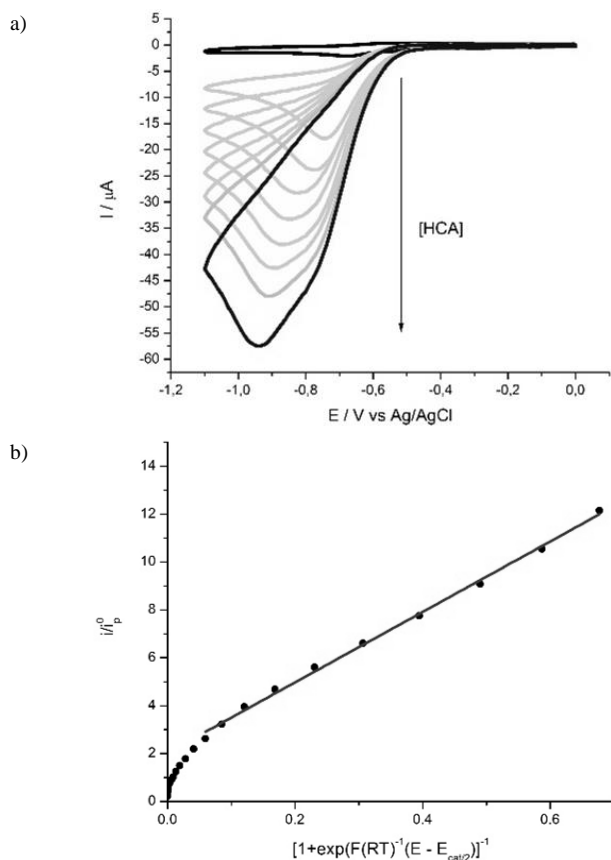


Figure 2. a) Cyclic voltammogram of $\text{Co}(\text{dbegH})_2\text{Cl}(\text{py})$ $0.100 \text{ mmol L}^{-1}$ in DMF 0.1 mol L^{-1} $[\text{NBu}_4][\text{PF}_6]$. Registered at a scan rate of 100 mV s^{-1} (black line) in the presence of 0.3 to 1.4 mmol L^{-1} of HCA (gray line). b) FOWA plot derived from cyclic voltammetry analysis, slope = 14.7 $R^2 = 0.99707$.

To identify the HCA dichlorination reaction products, gas chromatography (GC-MS) experiments were carried out sampling the headspace of the respective cobaloxime/chlorinated substrate solution (molar ratio 1:10) after 90 minutes of electrolysis (Fig. 3), found tetrachloroethene as the majority product.

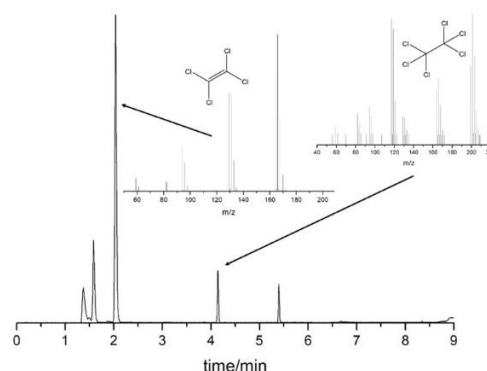
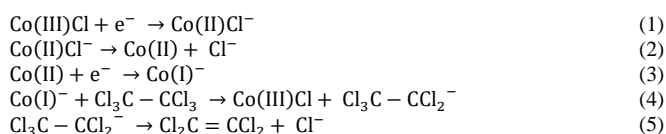


Figure 3. GC-MS electrolysis between $\text{Co}(\text{dbegH})_2\text{Cl}(\text{py})$ and HCA recorded in ACN.

A possible mechanism of the dechlorination process could begin with the sequential reduction of the cobalt center from the oxidation states III to I. This process has been described previously and involves an intermediate when the chloride ligand is lost. When the cobaloxime reaches the $\text{Co}(\text{I})$ state reacts with the organochlorine substrate causing the cleavage of the $\text{C}-\text{Cl}$ bond, releasing the reduced organochlorine and the oxidized catalyst, probably by an inner-sphere mechanism. Equations 1-5 describes this mechanism using HCA as a substrate. The glyoxime and pyridine ligands have been omitted for simplicity.



The kinetics of the process can be studied by estimating the observed rate constant (k_{obs}) from the relation between the cathodic current and the square root of the organochloride concentration, as presented in equation 1:

$$i_c = nFA[\text{Cobaloxime}]D^{1/2}k_{\text{obs}}^{1/2}[\text{RX}]^{1/2} \quad (1)$$

Where n is the number of electrons for the reaction ($n=2$), F is Faraday constant (96485 C mol^{-1}), A is the area of the electrode surface (0.072 cm^2), D is the diffusion coefficient (cm^2s^{-1}) and k is the apparent rate constant for the reaction ($\text{L mol}^{-1}\text{s}^{-1}$). Under pure kinetic conditions, the cyclic voltammogram should adopt an S-shaped response independent of the scan rate²⁹.

Although equation 1 allows obtaining the value of k_{obs} without complications, the catalytic voltammograms moved away from the ideal S-shape behavior, which could be attributed to side phenomena such as substrate consumption or catalyst inhibition^{30,31}.

In order to minimize the effect of these competitive secondary phenomena from the kinetic analysis we used the *foot-of-the-wave* analysis (FOWA) methodology developed by Saveant³² in which the observed rate constant is estimated by modeling the cyclic voltammogram near the foot of the wave where these factors play a small role and its shape is dominated by the catalytic reaction³³.

The FOWA analysis considers that the process occurs in multiple stages and all electron transfers occur at the electrode, the expression of the current is given by equation 2:

$$\frac{i_{\text{cat}}}{i_p^0} = \frac{2.24 \sqrt{\frac{RT}{F\nu}} k_{\text{obs}}}{1 + \exp\left(\frac{F}{RT}(E - E_{\text{cat}/2})\right)} \left(\frac{n_{\text{cat}}}{n_p^{3/2}}\right) \quad (2)$$

where k_{obs} is the observed rate constant, i_{cat} is the catalytic current (A), i_p catalyst current in the absence of substrate (A), E is the applied potential (V), $E_{\text{cat}/2}$ is the half-wave potential is defined as the point at which the homogeneous catalytic wave reaches half of its maximum current (V), n_{cat} number electrons transferred ($n=2$), n_p number of electrons of the catalyst ($n=1$), ν is the scan rate (Vs^{-1}), R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), and T is the temperature (K).

From the linear fit of i_p^0 as a function of $[1+\exp(F(RT)^{-1}(E-E_{cat/2}))]^{-1}$ a value of k_{obs} can be extracted. The FOWA plot derived from the analysis of the cyclic voltammogram is presented in Fig. 2b and in the supporting information for the other cobaloximes.

The rate constant of the catalyst in the dechlorination processes, k_{cat} , can be estimated by plotting k_{obs} obtained from the FOWA analysis versus the concentration of the substrate $[mol\ L^{-1}]$ considering a first-order dependence for both the catalyst and the organochlorine. The expression of this relationship is represented by equation 3:

$$k_{obs} = k_{cat}[RX] \quad (3)$$

Fig. 4 show the linear fit of k_{obs} of each cobaloxime versus the concentrations of HCA. Table 1 compiles the observed rate constants obtained by the FOWA analysis.

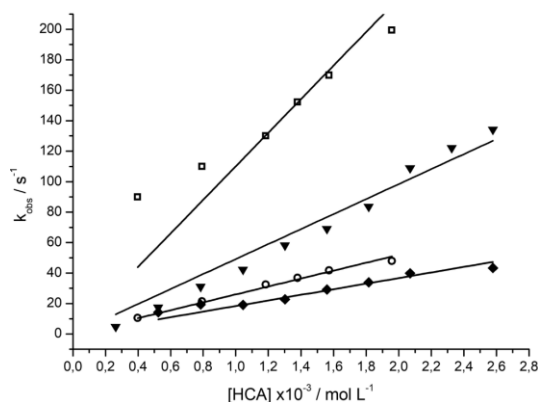


Figure 4. Dependence of the k_{obs} (s^{-1}) vs the concentration of HCA ($mol\ L^{-1}$), the data were adjusted to $k_{obs}=m[HCA] + 0$: Co(dmgh)₂Cl(py): slope = 110088 $R^2=0.97283$ (square); Co(chgh)₂Cl(py): slope = 49190 $R^2=0.99001$ (triangle); Co(dpgH)₂Cl(py): slope = 25979 $R^2=0.99756$ (circle); Co(dbegH)₂Cl(py) slope = 18348 $R^2=0.98918$ (diamond).

It can be seen that the value of the k_{cat} obtained by the FOWA analysis decreases when the potential of the redox pair Co (II/I) becomes more positive. This is congruent with the behavior reported for catalytic hydrogen evolution systems catalyzed by cobaloximes, where the presence of electron-withdrawing groups in the glyoxime ligand decreases the basicity of the cobalt center when it is reduced to Co (I), influencing its nucleophilic character.

Table 1. Reduction potentials and rate constants of the cobaloximes used in this study.

	$E_{1/2}$ (V) Co(II/I)	k_{cat} ($Lmol^{-1}s^{-1}$) FOWA analysis
Co(dmgh) ₂ Cl(py)	-0.91	1.10×10^5
Co(dpgH) ₂ Cl(py)	-0.69	2.59×10^4
Co(chgh) ₂ Cl(py)	-1.01	4.91×10^4
Co(dbegH) ₂ Cl(py)	-0,62	1.83×10^4

Fig. 5 shows the overlay plot of [Co(dbegH)₂Cl(py)] cyclic voltammograms when 1,1,1-trichloroethane, 1,2-dichloroethane, lindane and HCA, are added to the cobaloxime solution. This figure shows a difference in the catalytic current even at the same substrate concentration. For lindane, the catalytic currents were lower compared to HCA²⁷, and almost inexistent for 1,1,1-trichloroethane, 1,2-dichloroethane.

These last substrates have the same amount of carbons as HCA, but different number and position of the chlorine atoms. The analysis of the data suggests there is a relationship between the structure of the substrate and its ability to participate in reductive dechlorination reactions. This behavior has also been previously reported for cobalt porphyrins, which can only reduce local dihalides when they are in an antiperiplanar configuration³⁴. Probably this structural restriction also affects to the reaction of organohalides with cobaloximes.

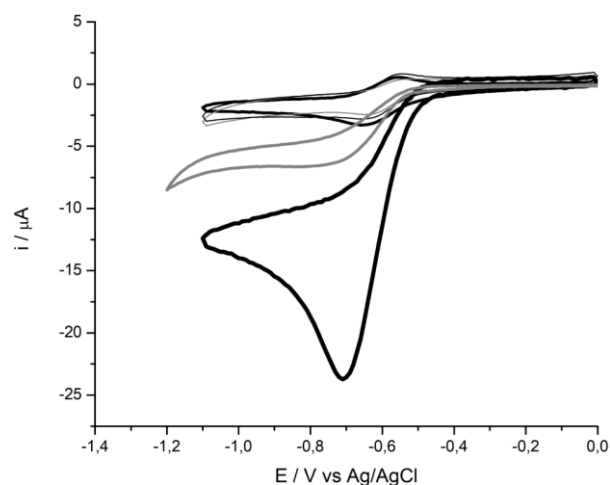


Figure 5. Cyclic voltammogram of Co(dbegH)₂Cl(py) 0.1 $mmol\ L^{-1}$ in DMF 0.1 $mol\ L^{-1}$ [NBu₄][PF₆]. Registered at a scan rate of 100 $mV\ s^{-1}$ (black line) in the presence of 1.0 $mmol\ L^{-1}$ of 1,1,1-trichloroethane (black line), 1,2-dichloroethane (gray line), lindane (gray bold line) and HCA (black bold line).

4. CONCLUSION

The catalytic dehalogenation of HCA using cobaloximes can be described using the FOWA analysis, which indicates a relationship between the activity of the catalyst, the Co(II/I) reduction potential and the structure of the glyoxime ligands.

Cobaloximes, nevertheless, apparently are efficient dehalogenation catalysts only of organochloride compounds which present vicinal chlorides.

ACKNOWLEDGMENTS

The authors acknowledge DIULS PI 17161; DIULS PR 17161, Plan de Mejoramiento Institucional en Eficiencia Energética y Sustentabilidad Ambiental ULS-1401.

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