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Catalytic dehalogenation of hexachloroethane using vic-dioximes nickel complexes

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ABSTRACT

The electrochemical degradation of hexachloroethane using bis(dimethylglyoximato) nickel (II), [Ni(dmgH)$_2$]; bis(diphenylglyoximato) nickel (II), [Ni(dpgH)$_2$]; difluoroborylbis (dimethylglyoximato) nickel (II), [Ni(dmgBF$_2$)$_2$]; and difluoroborylbis(diphenylglyoximato) nickel (II), [Ni(dpgBF$_2$)$_2$], is described. To achieve the degradation the nickel complexes were reduced by using electrochemical means. The chemical catalysis was studied using cyclic voltammetry by monitoring currents increases as the concentration of hexachloroethane was increase in solution. The rate constant of the dehalogenation process was estimated using *foot-of-the-wave* analysis (FOWA), obtaining: [Ni(dmgH)$_2$] 6.58 x 10^4; [Ni(dpgH)$_2$] 6.74 x 10^4; [Ni(dmgBF$_2$)$_2$] 7.06 x 10^4 and [Ni(dpgBF$_2$)$_2$] 1.0^8 x 10^4.

Key words: *Nickeloxime, Dehalogenation, Electrocatalysis.*

INTRODUCTION

Organochlorine compounds are widely used in industry, for vector control[1], solvents, the pharmaceutical industry[2], and various other fields. Unfortunately, their uncontrolled use, high persistence, and toxicity have led to several environmental issues. Numerous studies have confirmed that these substances can pose health problems[3], including alterations to the central nervous system[4], reproductive issues[5], and cancer[6].

Various methodologies have been employed to eliminate organochlorine contaminants, including biodegradation[7], zero-valence iron treatment[8], and the utilization of catalysts containing metal centers[9–11]. While these approaches have exhibited effectiveness, there is growing interest in the use of cost-effective and readily available first-row transition metals. Certain compounds such as porphyrins[12], tetraaza macrocyclic molecules[13–15], and pincer complexes[16] featuring first-row transition metals, have been utilized in reductive dehalogenation reactions. Our research group had focused on utilizing complexes based on vic-dioxime ligands for various reductive processes. Previously, we reported the application of cobaloximes as catalysts for hexachloroethane degradation[17], and we aimed to expand our exploration of such catalytic systems using other first-row metals.

In the field of catalytic degradation, precise assessment of reaction kinetics and mechanisms plays a pivotal role in advancing our understanding of catalytic processes and their environmental impact. Electrochemical techniques offer a potent tool for investigating these reactions, and the Foot-of-the-Wave Analysis (FOWA) technique, pioneered by Saveant[18], has emerged as an invaluable asset in this context. FOWA, a technique deeply rooted in electrochemistry, empowers researchers to extract intricate kinetic information by analyzing the current response near the onset of voltammetric waves. By concentrating on a specific fraction of the peak current, FOWA minimizes the influence of interfering processes, thereby providing insights into the reaction rate constants, electron transfer mechanisms, and standard rate constants.

In this study, the dehalogenation of hexachloroethane, was catalyzed by nickel glyoximes:

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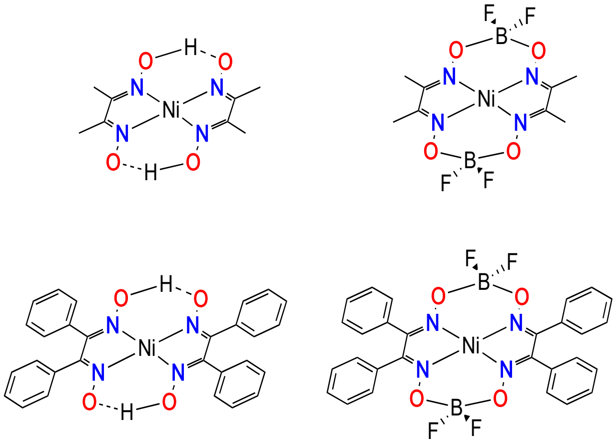
$[Ni(dmgH)_2]$, $[Ni(dpgH)_2]$, $[Ni(dmgBF_2)_2]$ y $[Ni(dpgBF_2)_2]$ (where dmgH: dimethylglyoximato; dpgH: diphenylglyoximato; $dmgBF_2$ is difluoroborylbis(dimethy-lglyoximato), and $dpgBF_2$ is difluoroborylbis (diphenylglyoximato)). The structure of these complexes is illustrated in Figure 1.

Figure 1. Structure of the nickel complexes.



EXPERIMENTAL

Materials and measurements

All chemicals were commercially available and used as received. $Ni(dmgH)_2$[19], $Ni(dpgH)_2$[20], $Ni(dmgBF_2)_2$, and $Ni(dpgBF_2)_2$[21], were prepared using previously described procedures.
The organochlorine compound employed in the catalytic degradation experiments was hexachloroethane.

Electrochemistry

Cyclic voltammetry experiments were conducted on a WaveDriver 40 DC Bipotentiostat Pine Research. A three-electrode single compartment cell was employed, consisting of a glassy carbon working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode.

The supporting electrolyte used was tetrabutylammonium hexafluorophosphate $[NBu_4][PF_6]$ at a concentration of 0.1 M. Before each measurement, the samples were degassed through nitrogen purging. Cyclic voltammograms were acquired using a 0.24 mM solution of nickel complexes. Small aliquots of the organochlorine compounds were added to increase their concentration from 0.2 to 20 mM.

RESULTS AND DISCUSSION

Figure 2 shows the cyclic voltammograms of the complexes $Ni(dmgH)_2$ (black line), $Ni(dpgH)_2$ (red line), $Ni(dmgBF_2)_2$ (blue line) and $Ni(dpgBF_2)_2$ (magenta line) registered in DMF 0.1 $[NBu_4][PF_6]$ at a concentration of 0.21 mM, 0.21 mM, 0.14 mM and 0.18 mM respectively. The half-wave potentials of the complexes are summarized in Table 1.

In this family of nickel compounds, the methyl substituents are replaced with phenyl groups, and additionally, the intramolecular hydrogen bond inherent in the glyoximato ligands is substituted with the difluoroboryl group. This alteration results in the formation of more robust macrocycles, a structural refinement that subsequently impacts the electrochemical properties of the Ni center.

The electrochemical assessment of both hexachloroethane and the nickel glyoxime complex was conducted using CV experiments. In the nickel complex, a process associated with the Ni(II/I) redox couples is observed. The reduction potentials of the nickel complexes are compiled and presented in Table 1. Variations in equatorial glyoxime ligand substituents significantly affected the reduction potential. Specifically, the substitution of alkyl groups with phenyl rings induced a shift in the reduction potential towards more positive values.

Dechlorination catalysis

The catalytic activities of the nickel complexes were investigated using hexachloroethane as a representative halogenated compound and employing the cyclic voltammetry technique. The hexachloroethane (HCA) substrate exhibits an irreversible reduction wave at -1.58 V *versus* Ag/AgCl[22].
According to literature, this reduction process involves electron transfer followed by bond rupture, which occurs in a single step. Owing to the tendency of the generated radical to undergo reduction more readily than the initial molecule, an overall 2 e- process was observed[23] (Figure 3).

Dehalogenation reaction can be catalyzed at more positive potentials by adding nickel complexes to the reaction medium. The observed behavior coincides with described in the literature

Figure 2. Cyclic voltammogram of $Ni(dmgH)_2$, $Ni(dpgH)_2$, $Ni(dmgBF_2)_2$ and $Ni(dpgBF_2)_2$.

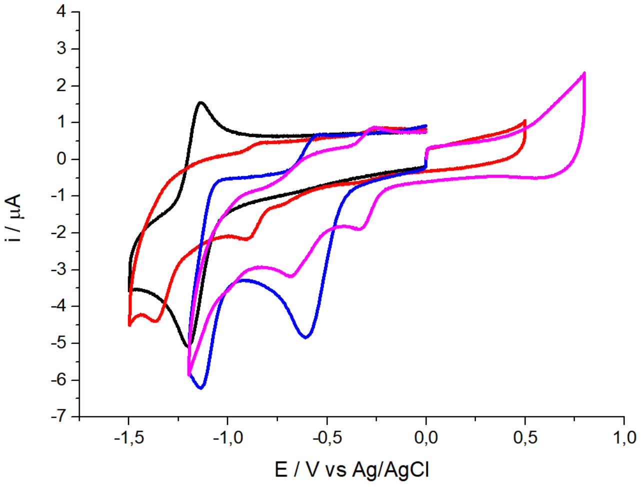


Figure 3. Dehalogenation mechanism of hexachloroethane.

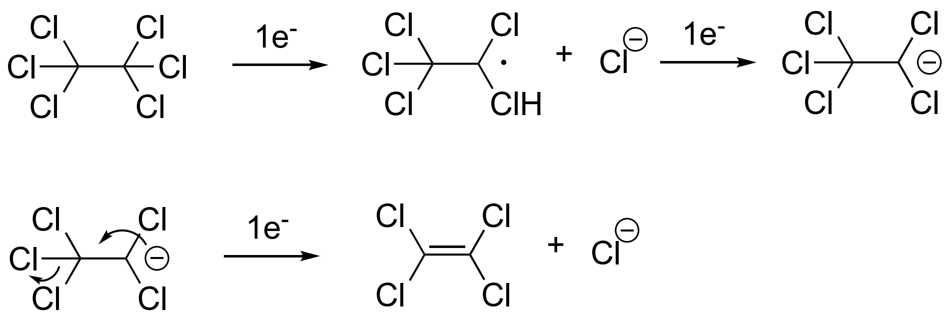
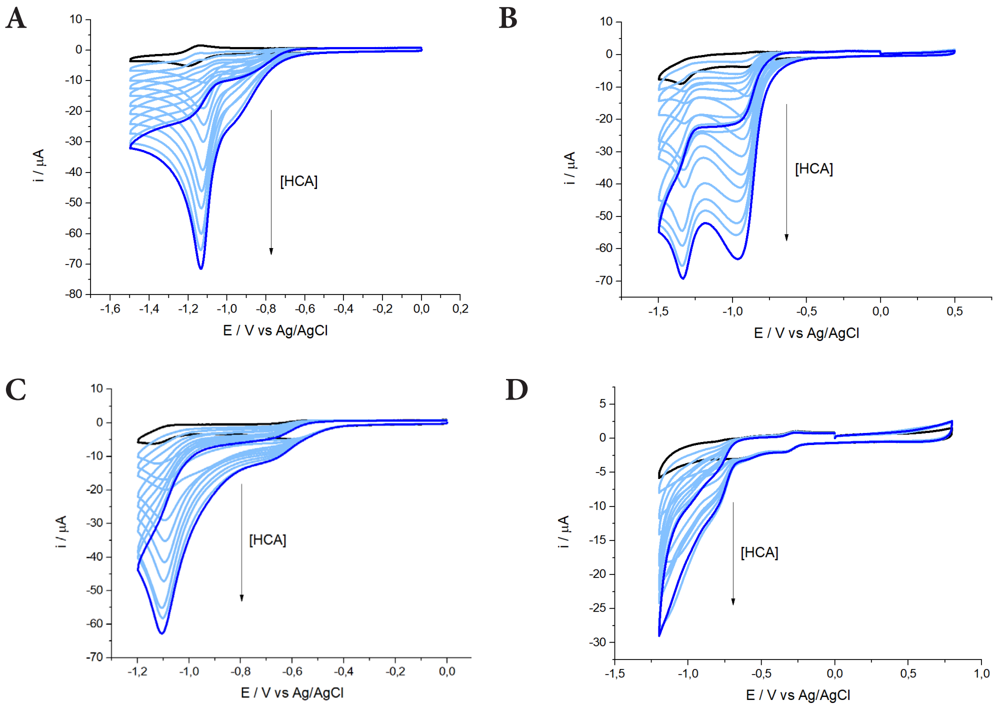


Figure 4. Cyclic voltammogram of (a) Ni(dmgH)$_2$ 0.21 mM, (b) Ni(dpgH)$_2$ 0.21 mM, (c) Ni(dmgBF$_2$)$_2$ 0.14 mM and (d) Ni(dpgBF$_2$)$_2$ 0.18 mM. All registered at a scan rate of 100 mV s^{-1} (black line) in DMF 0.1 M [NBu$_4$][PF$_6$] in the presence of 0.2 to 2.0 mM of hexachloroethane (blue line).

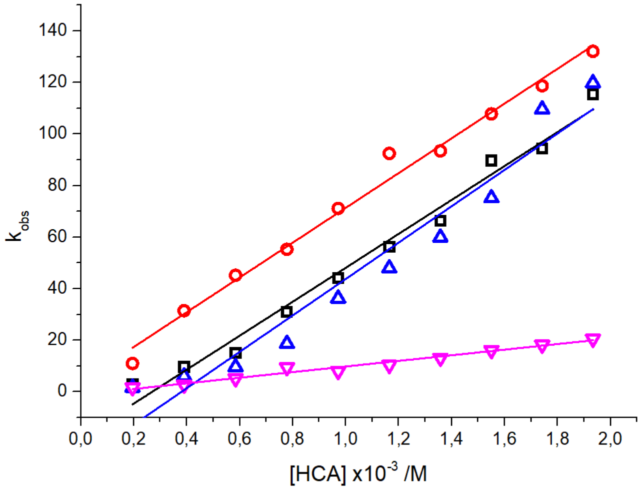


for similar electron transfer systems, particularly in hydrogen evolution processes[24]. The electrochemical responses of the nickel complexes and hexachloroethane are shown in Figure 3. In all cases, a surge in the current near the potential of the Ni redox couple was observed, indicative of electrocatalytic processes. The intensity and character of the electrochemical response are influenced by factors such as the structural attributes, reaction mechanisms, and position of the redox potential of the catalyst.

This trend is evident in Figure 4, where the intensity of the electrochemical response of Ni(dmgH)$_2$ complex is similar to that of the other nickel complexes. This difference can be attributed to the presence of electron-withdrawing phenyl groups, which elevate the potential of the Ni(II/I) redox couple to more positive values. To ascertain the kinetic parameters, we employed foot-of-the-wave analysis (FOWA), a method that facilitates the extraction of the observed rate constant by modelling the catalytic wave[25]. FOWA analysis operates on the premise that the process unfolds across several stages and all electron transfers take place at the electrode. The current is expressed by equation 1:

$$\frac{i}{i_p^0} = \frac{2.24 n_{cat}\sqrt{\frac{RT}{Fv}k_{obs}}}{1 + \exp\left(\frac{R}{RT}(E - E^0_{cat/2})\right)}$$

Figure 5. Dependence of the k_{obs} (s^{-1}) *versus* the concentration of HCA (M), the data were adjusted to k_{obs}=m[HCA] + c:[$Ni(dmgH)_2$] slope = 6.58x10^4 (black square); [$Ni(dpgH)_2$] slope = 6.74x10^4 (red circle); [$Ni(dmgBF_2)_2$] slope = 7.06x10^4 (blue triangle) and [$Ni(dpgBF_2)_2$] slope = 1.08x10^4 (magenta triangle).



where $_{kobs}$ is the observed rate constant, i is the catalytic current (A), i_p catalyst current in the absence of substrate (A), E is the applied potential (V), $E_{cat/2}$ is defined as the point at which the homogeneous catalytic wave reaches half of its maximum current (V), $_{ncat}$ number electrons transferred (n=2). From the linear fit of i/ip0 as a function of [1+exp(F(RT)$^{-1}$(E- $E_{cat/2}$)]$^{-1}$ a value of kobs can be extracted.

The rate constant for the hexachloroethane (HCA) dechlorination process was determined by modeling kobs against the substrate concentration, considering a first-order dependency for both the catalyst and organochlorine. Figure 5 illustrates the linear correlation between the kobs values of the nickel complexes with [HCA]. Interestingly, the FOWA constant was higher for [$Ni(dmgBF_2)_2$] than for [$Ni(dmgBF_2)_2$]. These values are listed in Table 1, which summarizes the electrochemical information obtained in this study.

To compare the activities of the nickel complexes used in our study with those of other similar catalytic systems, we generated a catalytic Tafel plot (Figure 5). The Tafel catalytic plot, as proposed by Costentin and Saveant, establishes the relationship between turnover frequency (TOF) and overpotential (η). This method enables an efficient comparison of catalysts based on their intrinsic properties, and the specific cell geometries used for bulk electrolysis[26]. The plot shows the logarithm of the TOF against the overpotential. As demonstrated elsewhere, the turnover frequency depends on the applied potential[27] as follows:

The value of TOF_{max} can be determined by examining the connection

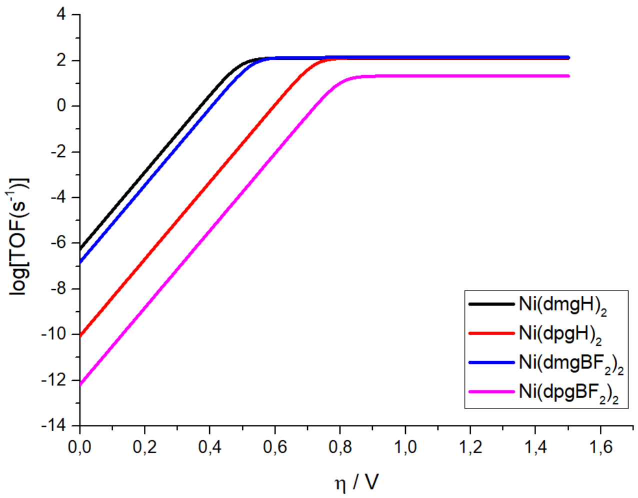
$$\eta_{cat} = \left|E_{A/C} - E_{cat/2}\right|$$

$$TOF = \frac{TOF_{max}}{\left(1 + \exp\left[\frac{F}{RT}\left(E_{A/C} - E_{cat/2}\right)\right] exp\left(-\frac{F}{RT}\eta\right)\right)}$$

between the rate constant and the concentration of the HCA. This relationship is described by the expression $TOF_{max}=k_{cat}$[HCA].

In this, α represents the transfer coefficient (α HCA= 0.27)[28], while η signifies the overpotential, E_{HCA} is the potential of the HCA and E_{cat} is the potential of the nickel complex.

Figure 6. Catalytic Tafel Plots for nickel complexes, [HCA]= 1.93 mM, E_{HCA}=-1.54 V.



Lexa *et al*[29]. reported the reduction of vicinal dibromoalkanes using iron, copper, and cobalt porphyrins by a typical “chemical catalysis” mechanism. It is possible to consider a similar system for nickel complexes with vic-glyoxime ligands, in which the electrochemical reduction of HCA occurs through an ECEC mechanism (E: electrochemical, C: Chemical), which has been proposed to form a transient adduct between the active form of the catalyst and the substrate, allowing the transfer of electrons, and the reduction of hexachloroethane to tetrachloroethylene.

The magnitudes of the constants found in this study are comparable to those of similar dehalogenation systems with polypyridine nickel complexes[30].

Table 1. AUC comparison between the amperometric response of the studied brands.

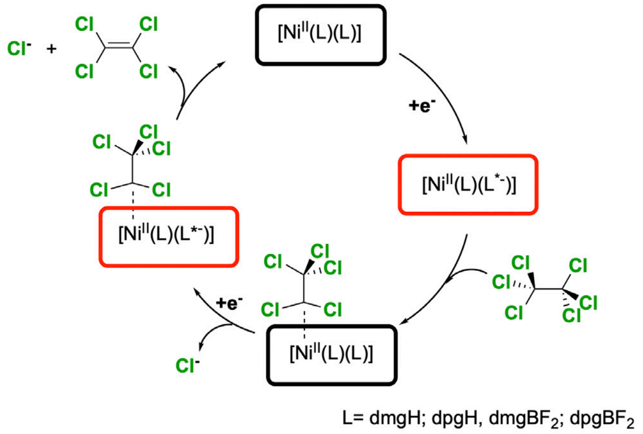
	$E_{1/2}$ Ni(II/I) (V)	FOWA kcat ($M^{-1}s^{-1}$)	Log(TOF(s^{-1}))
$[Ni(dmgH)_2]$	-1.17	6.58 x 10^4	2.12
$[Ni(dpgH)_2]$	-0.87	6.74 x 10^4	2.12
$[Ni(dmgBF_2)_2]$	-0,56	7.06 x 10^4	2.14
$[Ni(dpgBF_2)_2]$	-0,30	1.08 x 10^4	1.33

IR compensation, cell resistance DMF 0.1 mol l^{-1} $[NBu_4][PF_6]$ 275Ω

CONCLUSIONS

The presence of phenyl groups, or the incorporation of difluoroboryl substituents, affects the electrochemical properties of the nickel complexes, taking the potential of the Ni complex to more positive values.

Figure 7. Proposed mechanism for HCA dehalogenation.



Catalytic curves were obtained in cyclic voltammetry experiments by adding solutions with increasing concentrations of hexachloroethane. From FOWA analysis, it was possible to obtain the rate constants of the dehalogenation process. As the potential of the nickel redox couple was modulated to more positive potentials, the value of the observed constant gradually decreased.

Considering the observed results, nickel vic-dioxime systems are promising catalysts for the dehalogenation processes. Considering that the precursors are easy to obtain, and the synthesis is simple, new modifications are expected to improve the results obtained.

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