**ORMOSIL-entrapped copper complex as electrocatalyst for the heterogeneous dechlorination of alkyl halides**

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**Abstract**

The development of an efficient method for the de-halogenation of alkyl halides is essential to reduce the deleterious effects of these pollutants on the environment. Here we show that entrapment of an electro-catalyst in sol-gel electrodes yields efficient electrodes for this process. In this study Cu(1,4,8,11-tetra-aza-cyclo-tetra-decane)2+ was used as the active catalyst in the de-chlorination of CCl3CO2-. The major electro-catalytic product is oxalate while a minor product, depending on experimental conditions, is either glyoxalate or acetate. The efficiency of the electro-catalytic process depends on the nature of the precursors used to prepare the sol-gel matrix. The observed electro-catalytic current decreases when cyclic voltammetry is performed at high scan rates. This surprising result indicates that the mechanism of the electro-catalytic process is dependent on the scan rate. Plausible mechanisms at low and high scan rates are proposed.

Keywords: Electro-catalytic process; Sol-gel matrix; Cu Complex;

**Introduction**

Alkyl halides are the undesirable, toxic by-products of many industrial processes[[1-5]], such as those used to produce bromo-esters and the common flame retardants dialkyl-1-(trimethylsiloxy)alkylphosphonates, which are also used in medical systems. In addition, alkyl halides are also generated by widely used chlorine disinfection processes like those used in the treatment of drinking water [[6]]. Given the ubiquity of alkyl halides and their detrimental effects on the environment and on human health, a variety of methods for their efficient reduction have been investigated and published in the literature[[1-4, 7-19]]. The main approach to the treatment of these pollutants is their dehalogenation, for which both homogeneous and heterogeneous methods have been suggested[[20]]. The advantages of heterogeneous methods such as catalyst recycling, and the straightforward processes to separate catalysts from products, led us to develop a sol-gel-based process for electro-catalytic heterogeneous dehalogenation.

Heterogeneous catalysis, especially when it proceeds via an active species that is entrapped in a sol-gel matrix [[7, 21]], entails a number of advantages over homogeneous catalysis, including the capacity to recycle the catalyst. In homogeneous systems, in contrast, catalyst recycling is often not possible due to the difficulty entailed in separating the catalyst from the products of the process. In addition, solid-phase catalyst entrapment in a sol-gel often increases the efficiency of the active species relative to its activity in homogenous catalysis [[22-25]], and because the catalyst is entrapped in the inner pores of the sol-gel matrix, it is both protected and stabilized. The protective and stabilizing features of sol-gel matrices were illustrated by Avnir *et al.*, who showed that the entrapment of the enzyme alkaline-phosphatase in a sol-gel matrix enabled it to remain active at low pH values, that in homogeneous solutions would render them inactive [23]. This result is attributed to the low number of protons in the pores surrounding the enzyme, which protects the protein structures from the deleterious effects of low pH [22-24]. Another important advantage of the sol-gel process is the ability to control the nature of the matrix by varying the precursors used in its synthesis [21]. A recent study that used Ni(C10H24N4)2+ as a catalyst in amine oxidation showed that the diffusion rate of counter anions and/or of H3O+, an important measure of heterogeneous catalysis process efficiency, is affected by the precursors that are used [21].

The advantages of entrapment in sol-gels are applicable to a wide range of species, including inorganic molecules [25, 26]], metal nano-particles, metal-oxide nano-particles [[7, 27]], bacteria [[22]], yeasts [[28]] and enzymes [[22-24]]. Moreover, sol-gel matrices can be exploited in a variety of applications, for example, as catalysts [[7, 29-31]] and electro-catalysts [[32]], as ion exchange columns [[33, 34]], as electron exchange columns [[19, 26, 35]] and as slow release agents [[36, 37]].

The importance of developing an efficient treatment method for the alkyl-halide loads present in sewage prompted us to exploit the advantages of the sol-gel process in our investigation of the electro-catalytic de-halogenation of water-soluble alkyl-halides. To that end, we used a heterogeneous process in which tri-chloro-acetate was the representative alkyl-halide and Cu(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) functioned as the active species (Fig. S-1, in the supporting information (SI)). Copper complexes, especially Cu(I) complexes, are used as catalysts in a variety of reactions [[38, 39]], including the Ullmann reaction [[40, 41]], the Sandmeyer reaction [[42]], the Meerwein reaction [[43]] and the de-halogenation of Cl3CO2-[[39]] in homogenous systems. Due to the importance of copper complexes as catalysts, these reactions have been extensively investigated [.[[20, 38, 40, 41] However, less is known about the mechanisms of their activity in heterogeneous systems. Mono-valent copper complexes are known as catalysts for the dehalogenation of alkyl halides [[20, 39]]. Therefore, we decided to focus on the electro-catalytic de-halogenation of water-soluble alkyl-halides in a heterogeneous process that uses tri-chloro-acetate as the representative alkyl-halide and Cu(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane)2+, CuL12+, as the electro-catalyst (Fig. S-1, in SI). The structures for these compounds were reported earlier [[44]].

**Experimental**

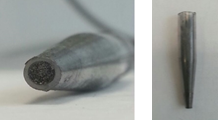
**Materials** – Analytical reagent grade tri-chlor-oacetic-acid, TCA, sodium perchlorate, perchloric acid, tetra-methoxy-silane, (TMOS), tri-methoxy-(phenyl)silane (TMPS), methyl-tri-methoxy-silane (MTMS), graphite, CuSO4 and 2,5,8,11-tetra-methyl-2,5,8,11-tetra-aza-dodecane (L1), acetonitrile and H3PO4 were purchased from Aldrich.

All solutions were prepared in de-ionized water that was further purified by passing it through a Milli Q Millipore setup with a final resistivity >10 MΩ/cm, TDW. Argon was used to de-aerate the solutions for at least 5 min. All reactions were studied at an ionic strength of 0.10 M that was maintained over the course of each reaction by the addition of NaClO4.

Spectra were measured using a UV-visible diode array spectrophotometer (Agilent 8453). Electrochemical experiments were performed using a multi-channel potentiostat (Metrohm Autolab) using Autolab hardware and GPES/Nova software. Three electrodes were used: Ag/AgCl as a reference electrode, Pt as a counter electrode, and sol-gel or glassy carbon (GC) as the working electrodes. HPLC analyses were performed using a Jasco XLC-3059AS with C18, Hypersil Gold column. The eluent composition was 90% TDW, 10% acetonitrile, and 0.2% H3PO4. The flow rate was 1.0 ml/min. ICP analysis was performed using an ICP-OES instrument (SPECTRO ARCOS). The method of CuL1+2 entrapment in sol-gel electrodes and matrices is described below.

**Electrode preparation** – Three kinds of sol-gel electrodes were prepared based on a procedure reported in the literature [[28, 45]] that we modified to obtain electrodes that were optimized for our experimental requirements. The electrodes differed from each other in terms of their precursors: Cu1 electrodes were made from a mixture of MTMS and TMPS, and Cu2 electrodes were made from TMPS. A third type of electrode made only from MTMS was also prepared, but these electrodes disintegrated shortly after their preparation, and therefore, electrochemical experiments were not performed with them. The amount of graphite, precursors (MTMS/TMPS), and CuL1+2 in each type of electrode was studied. The optimal conditions were chosen on the basis of the quality of the cyclic voltammetry measurements, the extent of leaching of the active species, CuL1+2, from the electrode, and the electrode drying time. The composition of the precursors affected the electrode drying time, which was significantly longer for the TMPS electrodes than for those prepared with MTMS probably due to the steric hindrance caused by the phenyl and methyl residues in the hydrolysis processes.

The ingredients were mixed on a plate until the mixture exhibited a creamy texture, after which it was inserted into a tube. The composition of each electrode is summed up in Table S-1, and Figure 1 shows an image of an electrode.

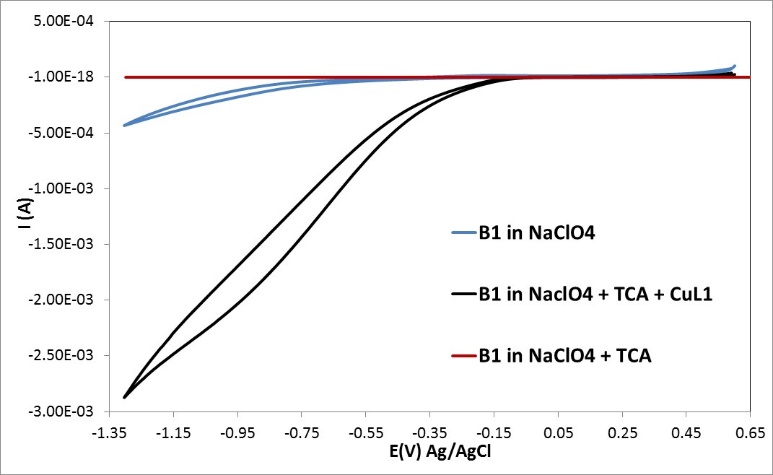


**Fig. 1** – ORMOSIL-graphite electrode -entrapped copper complex CuIIL1+2

**Results and discussion**

**Electro-catalysis**

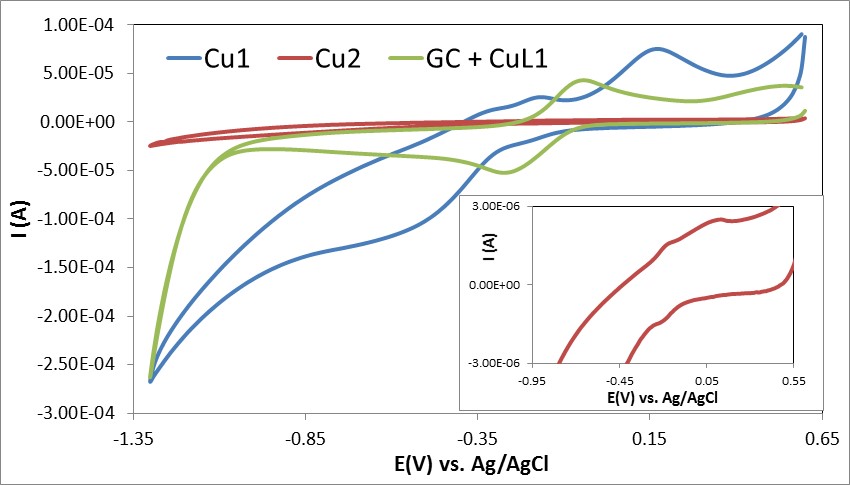
The activity of CuIIL12+ in the electrodes and the de-chlorination mechanism were studied using cyclic voltammetry. Control experiments were done using a glassy carbon (GC) or a sol-gel (B1 and B2) working electrode that did not contain CuIIL12+. The aqueous solution in the electrochemical cell included NaClO4 and/or TCA depending on the experiment. No de-chlorination reaction occurred in solutions that contained TCA without CuIIL12+ or in solutions that did not contain TCA (Fig. 2 for B1 and fig. S-2 for B2).

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**Fig. 2**. Cyclic voltammograms for B1 as working electrode. All the experiments were done at pH 7.0 and at a scan rate of 500 mv/s. **—** in solution containing 0.10 M NaClO4, **—** in solution containing 0.10 M NaClO4 and 0.20 M TCA, **—** in solution containing 0.10 M NaClO4, 0.20 M TCA, 1.87×10-3 MCuSO4, 5.60×10-3 ML1.

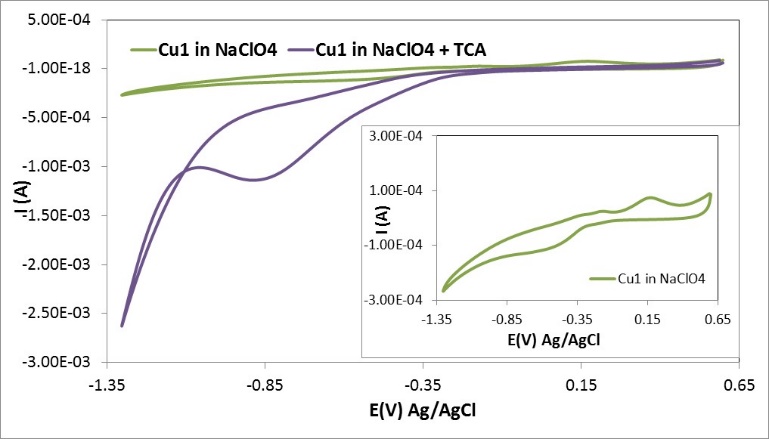
The voltammograms presented in Fig. 3 representing solutions without a substrate, (in this case TCA), and that use CuIIL12+-containing electrodes, the observed waves can be explained by the reduction oxidation reactions of CuIIL12+ (reactions 1 and 2). The redox potentials were taken from the literature at pH 7.0 [44]

|  |
| --- |
| (1) (CuIIL1) 2+ + e- (CuIL1)+ E= -0.157 V vs. Ag/AgCl, working electrode HDME [44] |
| (2) (CuIL1)+ + e - Cu0 + L1 E= -0.340 V vs. Ag/AgCl, working electrode HDME [44] |



**Fig. 3**. Cyclic voltammograms of the different working electrodes. All experiments were done in solutions that contained 0.10 M NaClO4 at pH 7.0 and at a scan rate of 500 mv/s. **—** Cu1-sol-gel electrode, **—** Cu2-sol-gel electrode **—** GC electrode 0.10 M NaClO4, 1.87×10-3 MCuSO4, 5.60×10-3 ML1.

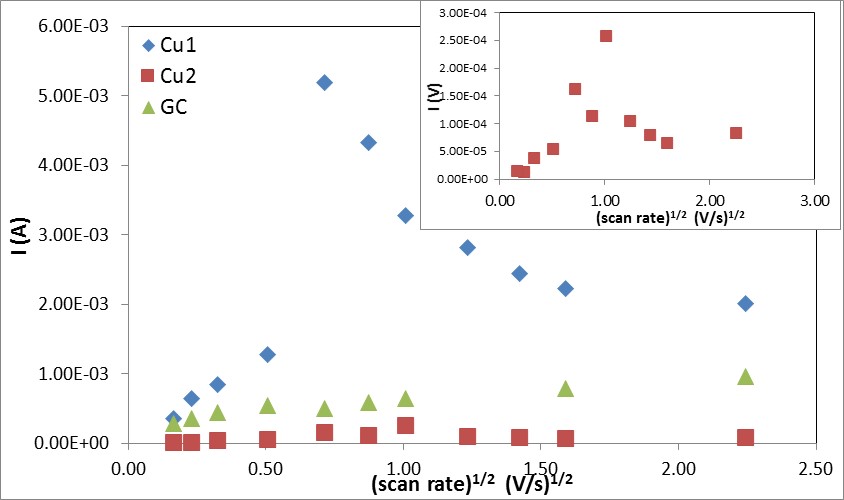
The inclusion in the sol-gel electrodes of copper and its absence from the solution shifted the redox potentials to somewhat lower values (Fig. 3). The current generated by the Cu1 (MTMS + TMPS) electrode was considerably larger than that generated by the Cu2 (TMPS) electrode. This result indicates that the composition of the precursors used to prepare the sol-gel electrodes significantly affects their electrochemical properties. Clearly, the presence of phenyl groups in TMPS, that are more hydrophobic and sterically demanding than the methyl groups in MTMS, affect the nature of the matrix, which in turn affects diffusion throughout the porous electrodes. Similar effects were reported when sol-gel electrodes were used for other electro-catalytic processes [21, 46]. The observed currents and redox potentials depend on the nature (i.e., [Cu1 (MTMS + TMPS) and Cu2 (TMPS)]) of the electrode used. Fig. 4 and Fig. S-3 present the cyclic voltammograms when the Cu1 and Cu2 electrodes were used as the working electrodes and the solution contained the substrate TCA. The observed increase in the current when TCA is in the solution indicates catalytic de-halogenation is taking place.

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**Fig. 4**. Cyclic voltammograms for Cu1 as working electrode. All the experiments were done at pH 7.0 and at a scan rate of 500 mv/s. **—** in solution containing 0.10 M NaClO4, **—** in solution containing 0.10 M NaClO4 and 0.20 M TCA

**Current - scan rate dependence**

To ascertain whether the de-chlorination reaction is a diffusion-controlled process, the dependence between current and scan rate was determined. The fit of the results to the Randles-Sevcik equation [47] is presented in Fig. 5. The linear dependence of the current to the scan rate up to ~500 mv/sec is clear for Cu1 due to the large catalytic current generated, but less so for Cu2, due to the considerably lower current generated, indicating that the process observed is a complex diffusion controlled process [21, 48].

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**Fig. 5.** – Current as a function of root of the scan rate. The currents were measured for **Cu1** at -0.90 V) and for **Cu2** at -0.80 V in solutions containing 0.10 M NaClO4, 2.0 M TCA, at pH 7.0 and for **GC** at -0.71 V) in a solution containing 1.87×10-3 MCuSO4, 5.60×10-3 ML1, 0.10 M NaClO4, 2.0 M TCA at pH 7.0.

With GC as the working electrode, the current-scan rate dependence reached a plateau at about ~500 mV/s. However,the dependence is less definitive because of the lower catalytic currents generated as compared to Cu1 (see Fig S-4).At the plateau, the rate-determining step is the chemical reaction rather than the electrochemical step. For the sol-gel working electrodes, however, a completely different behaviour is observed: the current initially increases with the scan rate, but above *~*500 mv/s, the trend reverses and the current begins to decrease as the scan rate continues to increase.increase. To the best of our knowledge, although a decrease in current as a function of an increasing scan rate is reported in the literature [49], the intriguing phenomenon observed here, an increasing and then decreasing current as a function of a continually increasing scan rate, has not yet been reported in the literature. This finding is suggested to be due to a competition between two mechanisms in the catalytic process, and the shift between the two mechanisms may be due to the rapid increase in the less positive potential. The following shift in the mechanism is proposed based on reactions previously reported [[38, 39]]. The first step in the catalytic process is:

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| --- | --- |
| (3) CuIL1+ + Cl3CCO2- → CuIIL12+ + Cl2CCO2.- + Cl- |  |

which is followed by:

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| --- | --- |
| (4) CuIIL12+ + Cl2CCO2.- → L1CuIII-CCl2CO2+ |  |

Reaction (3) was shown to be the first step in catalytic de-halogenation reactions by this type of CuIL1+ complex. Reaction (5) is usually slower than reaction (6)[39, 50], but because reaction (3) occurs in pores that are small relative to the solution environment, the radical Cl2CCO2.- that forms in proximity to CuIIL12+ is expected to react with the latter as no CuIL1+ is present in the immediate vicinity[38, 39].

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| --- | --- |
| (5) CuIIL2+ + R. → LCuIII-R2+ |  |
| (6) CuIL+ + R. → LCuII-R+ |  |

The final products will be formed via the decomposition of the transient complex L1CuIII-CCl2CO2+, see below. However, at sufficiently high scan rates, one of two possibilities arises:

1. The most probable is that the transient L1CuIII-CCl2CO2+ complex is electrochemically reduced:

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| (7) L1CuIII-CCl2CO2+ + e- → L1CuII-CCl2CO2 |  |

Or

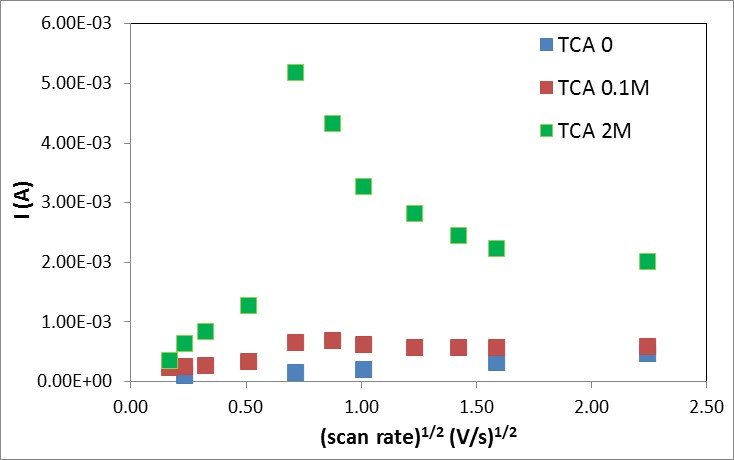
1. Prior to reaction (4), the CuIIL12+ formed in reaction (3) is electrochemically reduced to CuIL1+, which reacts with the radical anion Cl2CCO2.- to form the transient complex L1CuII-CCl2CO2.

In both cases, the transient complex formed at the higher scan rate is L1CuII-CCl2CO2. It is well known that transient LCuII-CCl2CO complexes have considerably longer lifetimes than do LCuIII-CCl2CO complexes [[39]], which explains the lower currents observed at the higher scan rates.

Note that considerably different catalytic currents were obtained when the different sol-gel electrodes were used. In the case of the Cu1 electrode (MTMS + TMPS), the observed current was considerably higher than that obtained with the Cu2 (TMPS) electrode. This finding is attributed to the effects of the larger size and more hydrophobic nature of the phenyl relative to the methyl substituents, properties that affect the substrate and counter ion diffusion rates in the meso-pores of the sol-gel matrices. Analogous observations were previously reported when sol-gel electrodes were used in different electrochemical processes [[21, 46]]. These results clearly indicate that the precursors used to prepare the electrodes significantly affect catalytic process efficiency.

**Effect of substrate concentration on current**

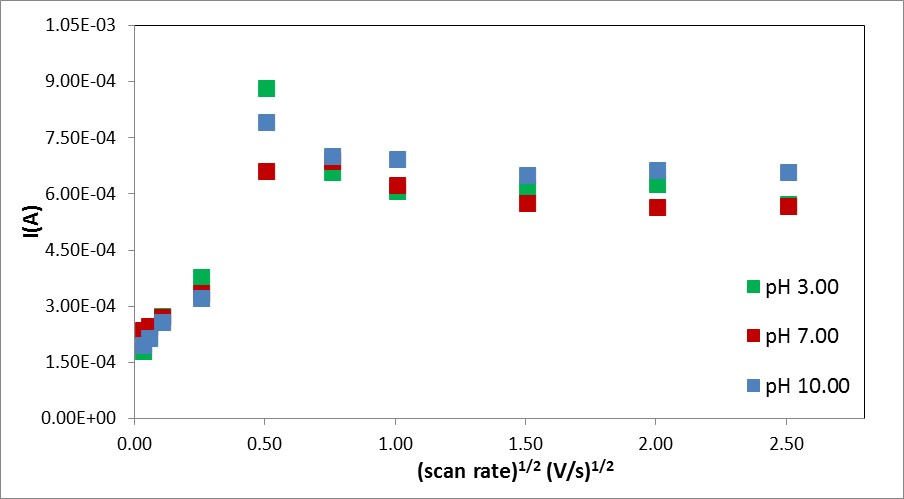
The effect of substrate concentration on current was studied. The results presented in Fig. 6 indicate that, as expected, the current increased with an increase in the concentration of TCA.



**Fig. 6**. Current as a function of the root of the scan rate. Experiments were performed with the Cu1-sol-gel electrode as the working electrode at -0.90 V in a solution containing 0.10 M NaClO4 at pH 7.0 and with different concentrations of TCA.

**pH effect on current**

CuIIL2+ entrapment was performed by mixing its aqueous solution at pH 7.0 with the precursor/precursors. As the structure of CuIIL2+ is known to vary with pH [[44, 51]] (Fig. S-1), and the complex is unstable in acidic solutions, the effect of the pH of the solution being electrolyzed was studied. The results are summarized in Fig. 7.



**Fig. 7**. Current (at E -0.90V) as a function of the root of the scan rate at different pH values. The experiments were performed using the Cu1-sol-gel electrodes as working electrodes in solutions containing 0.10 M NaClO4 and 0.10 M TCA.

The results indicate that pH had no effect on current , a finding that is probably due to the stabilizing effect of the sol-gel matrix on catalysts entrapped within [23, 52]. This might be partially due to the small number of protons in the pores near the complex, even in acidic solutions [23], We thank the reviewer for suggesting this point. However, as CuL2+ decomposes when even one or two amines are protonated, the stability of CuL2+ in the matrix cannot be solely attributed to this.

**Product identification**

Though products formed during the electrochemical experiments were present in concentrations too small to measure quantitatively, oxalate and perhaps glyoxalate were definitively identified. To validate that we correctly identified our products, the catalytic reduction was performed by another method, the catalytic reduction of TCA by ascorbate in the presence of CuIIL2+ (methods described in section S-1 in the SI). CuIIL2+ was entrapped in three kinds of sol-gel matrices, the details for which are included in section S-2 in SI. (The results indicate that the matrix composition does not affect the results). The products of the catalytic process were identified by HPLC. The results indicate that oxalate and maybe some glyoxalate were formed. (HPLC chromatograph is included in Fig. S-5 in SI).

The formation of oxalate as the major product is attributed to the following plausible mechanism: The L1CuIII-CCl2CO2+ formed in reaction (4) is expected to decompose via:

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| --- | --- |
| (8) L1CuIII-CCl2CO2+ + H2O → CuIL1+ + HOCCl2CO2- + H+ |  |

Reaction (8) is analogous to the mechanisms of decomposition reported for a variety of L1CuIII-R complexes [[38, 39]]. Reaction (8) will be followed by:

|  |  |
| --- | --- |
| (9) HOCCl2COO- → HCl + C(O)ClCOO− |  |
| (10) C(O)ClCOO- + H2O → -OOCCOO- + HCl + H+ |  |

The glyoxalate is formed via the decomposition of the L1CuII-CCl2CO formed in reaction (7) via the following mechanism:

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| --- | --- |
| (11) L1CuII-CCl2CO2 + H2O → CuIIL12+ + HCCl2CO2- + OH- |  |

Reaction (11) is analogous to the mechanisms of decomposition of many L1CuII-R complexes [[38, 39]], those that do not decompose via hemolysis [38, 39]. Reaction (11) will be followed by:

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| --- | --- |
| (12) CuIL1+ + HCl2CCO2- → CuIIL12+ + HClCCO2.- + Cl- |  |
| (13) CuIIL12+ + HClCCO2.- → L1CuIII-HCClCO2+ |  |
| (14) L1CuIII-HCClCO2+ + H2O → CuIL1+ + HOCHClCO2- + H+ |  |
| (15) HOCHClCO2- → HC(O)CO2- + HCl |  |

If under the electrochemical conditions reaction (13) is replaced by:

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| (16) L1CuIII-HCClCO2+ + e- → L1CuII-HCClCO2 |  |

where reaction (16) is analogous to reaction (7), then the final product would be acetate instead of glyoxalate.

**Active species leaching**

Leaching of the active species, CuIIL1+2, from the electrodes was studied spectrophotometrically and by ICP. The results, which are described in detail in section S-3 in the SI, indicate that if any leaching occurred, it was minimal. This outcome can be explained by the formation of hydrogen bonds between the ligand and the matrix residue, which is supported by similar findings reported in the literature [[21, 26, 46]].

**Conclusions**

Our results describe a completely new phenomenon – namely, the observed decrease in electro-catalytic current with increasing cyclic voltammetry scan rates – that to the best of our knowledge, has not yet been published in the literature. A decrease in the current with an increasing scan rate was reported for another mechanisms[49]. However, to the best of our knowledge, in no system was a decrease in the current shown preceded by an increase in the current. Our observation indicates that the mechanism of the electro-catalytic reduction changes with increasing scan rate.

The results presented herein indicate that the CuIIL12+ complex entrapped in a sol-gel matrix is an efficient electro-catalyst for the de-chlorination of TCA. We suggest two possible mechanisms for this reaction: in one, reactions (4) & (8)-(10), the predicted product is oxalate, while in the other, reactions (7) & (11)-(15), the predicted product is glyoxalate. If the electro-catalytic process in the latter mechanism is performed under a sufficiently negative potential, reaction (16) replaces reaction (14), and the expected product is acetate.

In addition, the results clearly indicate that the use of the electrode consisting of the sol-gel matrix is a good alternative to the homogeneous electro-catalytic process. Furthermore, the sol-gel matrix protects the CuIIL12+ complex from decomposing at pH values that can render the complex unstable in the homogeneous solution.

The results also show that the nature of the precursors used to prepare the sol-gel electrode has a considerable affect on electrode efficiency. These results have far-reaching implications in terms of catalytic process control and active species recycling.

**Acknowledgements**

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