

Short Communication

Mechanism and Cyclic Voltammetry of $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ in Aqueous 0.2MNaClO_4

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The electrochemical studies of bis (ethylenediamine)copper(II)per chlorate - $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ in aqueous 0.2M NaClO_4 at glassy carbon electrode (GCE) has been carried out using cyclic voltammetry. It is observed that in the first cycle reduction peak c_1 assigned to $\text{Cu}(\text{I})$ complex specie appears followed on the reverse scan by complicated oxidation peaks. On second and subsequent cycles a preceding irreversible reduction peak c_1' appears with no change in the oxidation peaks. The intensities of both cathodic and anodic peak current are also increased with increasing scan rate consistent with Randle-Sevcik equation. A linear behaviour of cathodic peak current versus square root of scan rate with a positive intercept indicates that the electrochemical processes are not fully diffusion controlled. It is proposed that electron charge transfer steps are preceded by chemical reactions, (CECE mechanism).

Keywords: Cyclic voltammetry, Redox reaction, Aqueous media, Bis(ethylenediamine)copper(II) perchlorate, mechanism

1. INTRODUCTION

Understanding the mechanism of electrochemical reactions is important from the basic science point of view as well as for the development of electrochemical applications such as batteries, solar and fuel cells [1]. Electrochemistry provides convenient methods for studying mechanism and kinetics[2]. Electron transfer processes, whether homogeneous or heterogeneous, have on the one hand, a finite rate whose value dependent on the activation parameters [3,4,5] and on the other, that they are often preceded and followed by chemical reactions (mechanism) [6,7,8]. The role of copper proteins in biological electron transfer processes has stimulated a high level of interest in the kinetics and mechanism of copper redox reaction [9]. Reviews of $\text{Cu}(\text{II})$ electrochemistry and typical kinetic parameters of copper(II) reduction has been presented [10,11,12]. Ethylenediamine as a classic chelate has metal complexes that have been investigated and their structures solved [13]. However, the mechanism of its complexes of the type $\text{Cu}(\text{en})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ have earlier not been investigated. Recently

one of these authors investigated the mechanism of solid $\text{Cu}(\text{en})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($n = 0$ for $\text{X} = \text{ClO}_4^-$, NO_3^- , SCN^- and $n = 1$ for Br^-) in dimethylsulfoxide, acetonitrile, and dimethylformamide in 0.1M tetrabutylammonium per chlorate using cyclic voltammetry have earlier been investigated and the result showed CECE mechanism[14].

Since the nature of solvent has considerable influence on the composition and stability of complexes formed [15], these authors have therefore extended the study of mechanism of solid complexes of $\text{Cu}(\text{en})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ to that of $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ in aqueous media using cyclic voltammetry as it is the most effective and versatile technique in the diagnosis of complex electrode mechanisms in the present work.

2. EXPERIMENTAL

2.1 materials

Analytical reagent grade $\text{Cu}(\text{ClO}_4)_2$ and NaClO_4 were used for the preparation of $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ and 0.2M NaClO_4 respectively. The aqueous solvent was double distilled water. Ethylenediamine, (en) was obtained from Aldrich (USA).

2.2 Methods

$\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ was prepared according to the method as reported in [16]. The Glassy carbon electrode (GCE) was polished with a fine alumina powder sprinkled on a cloth wetted with double distilled water in an 8- shape method for about 3-8 minutes and the shiny black mirror like electrode surface was thoroughly washed with double distilled water.

All the cyclic voltammetric experiments were done in an inert atmosphere achieved by purging the cell solutions with nitrogen gas for about 20 minutes and maintained over the cell solution during the recording of the voltammogram. The nitrogen gas was previously purified by bubbling through alkaline vanadous sulphate solution and passing through a calcium sulphate drying tube. Freshly prepared solutions were used in carrying out the experiments at 25⁰C in aqueous 0.2M NaClO_4 supporting electrolyte. The scan rates were varied from 10 to 300 mVs^{-1} .

2.3 Equipments

The oxidation reduction potentials were obtained with a BAS model CV-IB (Indiana USA) cyclic voltammograph instrument having an electrochemical cell with a three electrodes system. The working electrode was a glassy carbon electrode. Platinum wire was used as auxiliary electrode, while a saturated calomel electrode (SCE) as a reference electrode with $E^0 = 0.242 \text{ V}$ vs NHE. The voltammogram (CV) was recorded on an X-Y recorder.

3. RESULTS AND DISCUSSION:

Figure 1 shows the cyclic voltammogram (CV) of 1.0×10^{-3} M $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ in aqueous 0.2M NaClO_4 carried out at GCE and at 25mVs^{-1} .

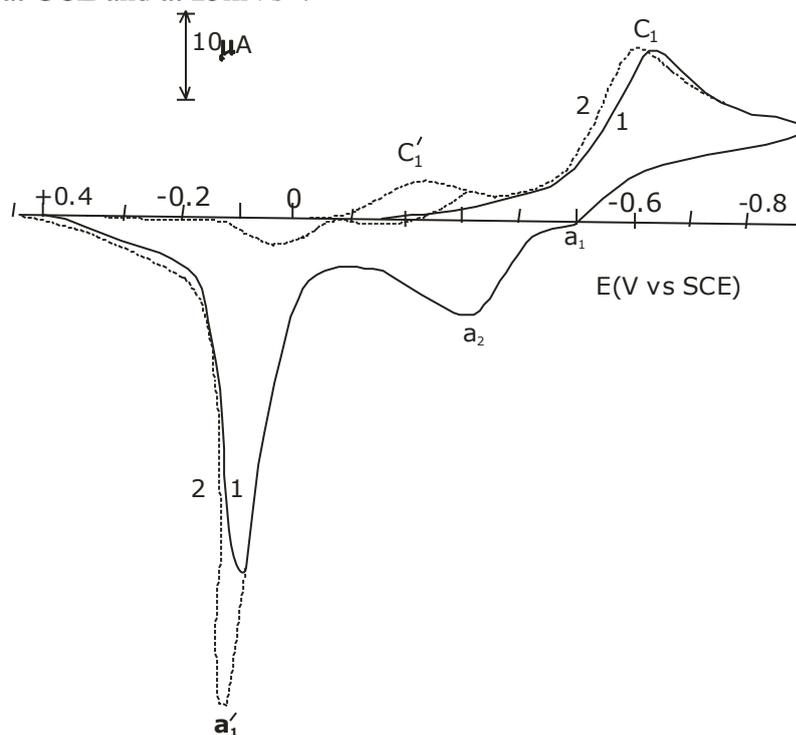
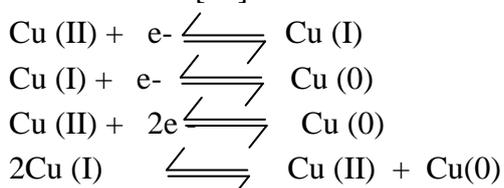


Figure 1: Cyclic voltammogram of 1mM $\text{Cu}(\text{en})_2\text{ClO}_4$ in aqueous 0.2M NaClO_4 at scan rate of 25mVs^{-1} at GCE.

Within the potential windows of +0.50 to -0.80V vs SCE, the CV exhibited a reduction peak c_1 at about -620mV followed in the reverse scan by three anodic peaks a_1 at -500mV, a_2 and a_1' located around -300 and +110 mV respectively. In the second cycle, a reduction peak c_1' appears at about -200mV. Peaks c_1 and a_1 at best represent a quasi-reversible couple attributable to $\text{Cu}^{2+/+}$ redox reaction with a formal potential $\approx -560\text{mV}$.

The anodic peak current I_{pa_1} is very small ($4.0\mu\text{A}$) compared to the cathodic current counterpart I_{pa_2} ($5.0\mu\text{A}$) and $I_{pa_1'}$ ($24.0\mu\text{A}$). Also, the anodic peak $I_{pa_1'}$ is very intense with a strong peak current attributable to demetallation of Cu (0) directly to Cu (II).

It is established that Cu (II)/Cu (I) electron transfer couple is very distinctive. In polar solvents, Cu(II) complexes exists mainly as five or six coordinate tetragonal species, where however, Cu(I) complexes expectedly favour four (tetrahedral) or lower coordination numbers. Electron transfer between Cu (II) and Cu(I) would therefore be accompanied by major structural and stereo chemical changes[17]. The feature of aqueous chemistry of copper can be summarized by the following equilibrium reactions [17]



The stability of Cu (II) and Cu(I) ions depends highly on the environment in solution[17]. Stability in aqueous conditions depends on the hydration energy of the ions when they are bonded to water molecules. The Cu(II) ions has a greater charge density than the Cu(I) ion therefore, forms much

stronger bonds releasing more energy. On the other hand Cu (I) is significantly stable in the presence of complexing ligand such as Cl⁻ [17,18] and in non aqueous media [17,19]. In non aqueous solvents, the stability of Cu (I) is due to the fact that these solvents solvate Cu (II) less strongly than does water. However, this theory does not seem to hold good for Epc₁ - that is the oxidation of Cu(I) complex specie -Cu(en)₂⁺ in the vicinity of the glassy carbon electrode to Cu(II)complex specie -Cu(en)₂²⁺.

Table 1. Cyclic voltammetric parameters for Cu(en)₂ClO₄ in aqueous 0.2M NaClO₄

| Scan rate (mVs ⁻¹) | Epc ₁ (mV) | Epa ₁ (mV) | Epa ₁ ' (mV) | Ipc ₁ (μA) | Ipa ₁ (μA) | Ipa ₁ ' (μA) | ΔEp (mV) | Ipa ₁ /Ipc ₁ |
|--------------------------------|-----------------------|-----------------------|-------------------------|-----------------------|-----------------------|-------------------------|----------|------------------------------------|
| 10 | -595 | -475 | +90 | 12.0 | 2.5 | 49.5 | 120 | 0.21 |
| 25 | -620 | -500 | +110 | 15.0 | 4.0 | 24.0 | 120 | 0.27 |
| 50 | -630 | -500 | +100 | 17.5 | 5.0 | 19.5 | 130 | 0.38 |
| 100 | -640 | -495 | +100 | 22.0 | 7.5 | 22.5 | 145 | 0.34 |
| 150 | -645 | -490 | +110 | 25.0 | 9.0 | 25.0 | 150 | 0.36 |
| 200 | -650 | -490 | +120 | 28.0 | 10.5 | 24.0 | 160 | 0.38 |
| 250 | -660 | -480 | +125 | 30.0 | 11.5 | 20.5 | 180 | 0.38 |
| 300 | -670 | -470 | +130 | 32.5 | 13.5 | 34.0 | 200 | 0.40 |

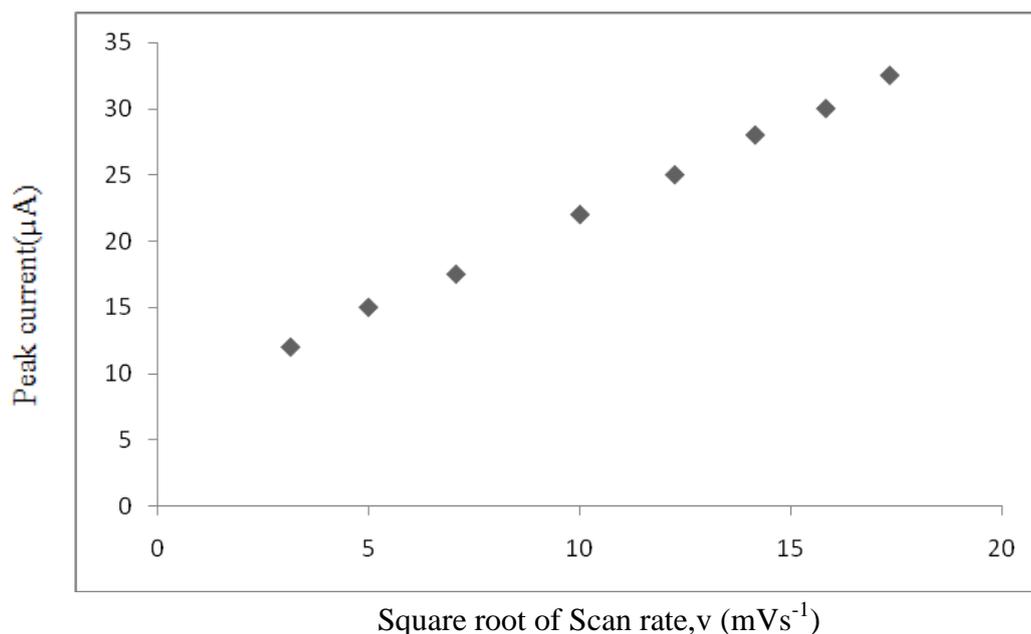


Figure 2. Dependence of peak current Ipc₁ with square root of scan rate for Cu(en)₂ClO₄

There is a strong probability of dissociation of Cu (I) complex specie as follows:

$2[\text{Cu(en)}_2]^+ \rightleftharpoons [\text{Cu(en)}_2]^{2+} + \text{Cu(0)}$, thus greatly reducing the concentration of Cu(en)₂²⁺ at the surface of the electrode(GC E) as indicated by the less intense anodic peak current Ipa₁ while anodic peak a₂ indicates the oxidation of Cu(0) to Cu(I).

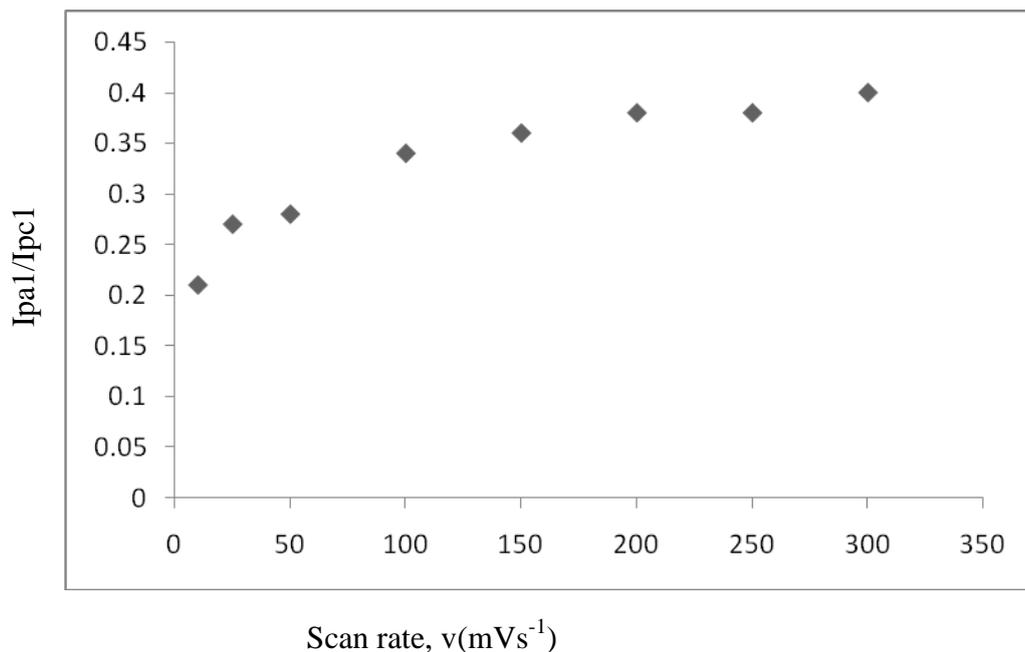


Figure 3. Dependence of peak current ratio I_{pa1}/I_{pc1} on scan rate of 1mM $\text{Cu}(\text{en})_2\text{ClO}_4$ in aqueous 0.2M NaClO_4

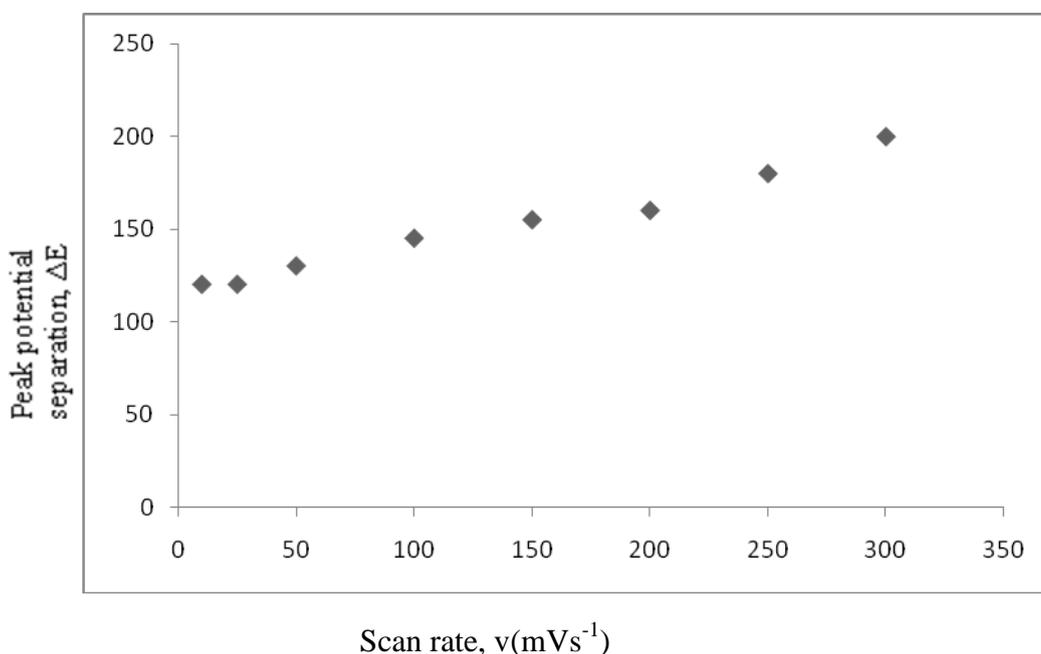


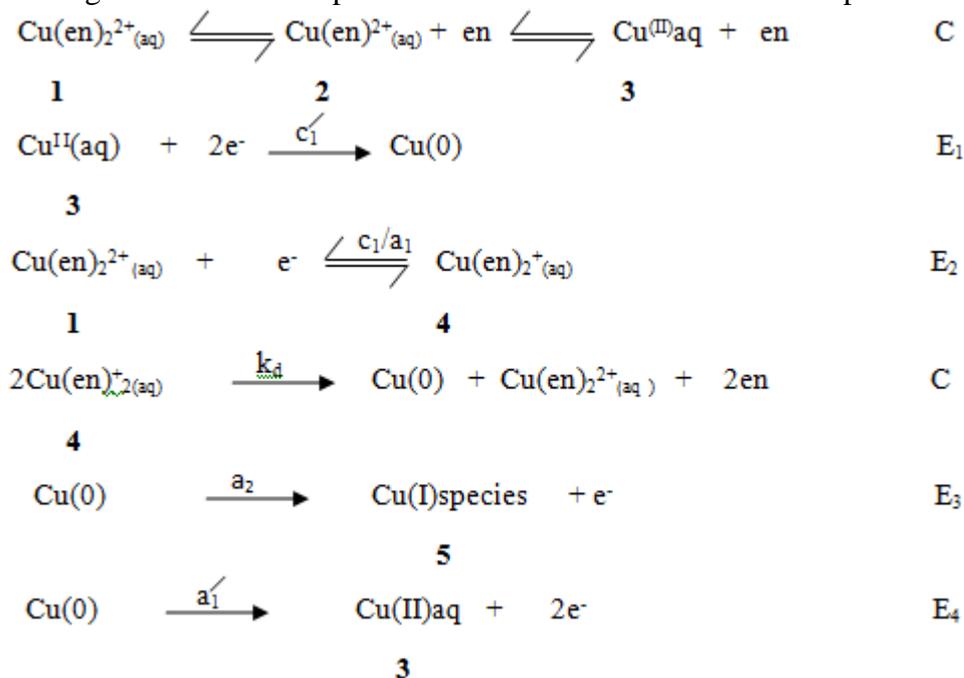
Figure 4. Variation of peak potential separation with scan rate of 1mM $\text{Cu}(\text{en})_2\text{ClO}_4$ in aqueous 0.2M NaClO_4

Also at the switching potential E_{λ} of -0.305V, the reverse anodic peak a'_1 is related to the cathodic peak counterpart c_1' indicating that c_1' is a Cu(0). Also the appearance of c_1' at second cycle and its disappearance at $v \geq 50 \text{ mVs}^{-1}$ indicates that a solvated Cu(II) ion is chemically formed in solution and its rate of formation is kinetically slow. This $\text{Cu}^{\text{II}}_{(\text{aq})}$ ion is therefore reduced to Cu (0) at c_1' (-200mV).

The voltammetric parameters are gathered in Table 1. With increasing of scan rate, cathodic as well as anodic current increases (exception I_{pa1}) and cathodic potential have shifted towards negative values, while anodic peak potential move towards more positive or less negative values.

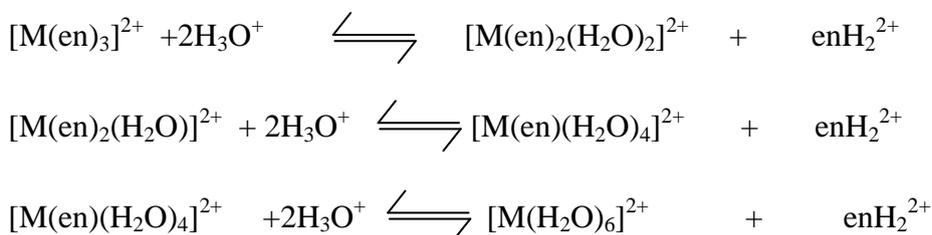
These observations suggest that the electrode process is diffusion controlled. The value of I_{pa1}/I_{pc1} is $\ll 1.0$ (0.21-0.40). This may be due to the chemical reaction taking place following the reduction of Cu(II) complex to Cu(I) complex specie and during the oxidation of Cu(I) complex specie to Cu(II) complex specie. This also indicates that the electron transfer is followed by chemical reaction [20]. However, the plot of cathodic peak current (I_{pc1}) versus square root of scan rate v (mVs^{-1}) has a linear relation with a positive intercept (Fig. 2). This observation indicates the fact that the electrode process is not fully diffusion controlled but that the electron transfer is preceded by chemical reaction [20, 21]. The ratio of the oxidation peak current to its corresponding reduction counterpart, I_{pa1}/I_{pc1} increases with increasing scan rate (Fig.3). Also the peak potential separation, ΔE_p is increased with the variation of scan rate (Fig.4). These suggest a quasi- reversible redox process rather than reversible reaction.

The following scheme would explain most of the observed data and dependence:



The above reaction scheme strongly indicates that one chemical reaction step precedes and the other is interposed between electron transfer steps – CECE [20,22, 23] mechanism for the redox process of $1.0 \times 10^{-3} M \text{Cu(en)}_2(\text{ClO}_4)_2$ in aqueous media.

Ahmed and Wilkins [24,25] have studied the kinetics of dissociation of mono-, bis-, and tris (ethylenediamine) metal complexes in aqueous solution over a wide range of pH and also in methanol. The equilibria involved in these processes can be represented as:



Similar but not related mechanism involving two electro reduction and two chemical steps (CECE) had been proposed for the electro reduction of Zinc(II) in aqueous solutions[26] from the

measurements of different solvent activity. More recently, polarographic, kinetic and voltammetric results of the reductive cleavage of chlorine from 6-chloronicotinic acid on mercury electrode shows CECE process [27]. Most recently, a mechanism similar and related is the study of complexes of $\text{Cu}(\text{en})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($n=0$, for $\text{X}=\text{ClO}_4^-$, NO_3^- , SCN^- and $n=1$ for Br^-) in some nonaqueous solvents [14].

4. CONCLUSION

The mechanism and cyclic voltammetry of bis(ethylenediamine)copper(II) perchlorate - $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ has been carried out in aqueous 0.2M NaClO_4 . The voltammogram shows two cathodic peaks and three anodic peaks. The mechanistic pathway shows that one chemical reaction step precede while the other is interposed between electron transfer steps, giving an CECE mechanism. Similar related mechanistic result was found in the study of complexes of $\text{Cu}(\text{en})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($n=0$, for $\text{X}=\text{ClO}_4^-$, NO_3^- , SCN^- and $n=1$ for Br^-) A mechanism similar but not related is observed in the electro reduction of Zn(II) in aqueous solution [26] and the reductive cleavage of chlorine from 6-chloronicotinic acid [27].

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