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Electrochemical Properties of Closo-2,3-dicarbaundecaborane in Dichloromethane at a Glassy Carbon Electrode using Potentiostatic, Galvanostatic and Digital Simulation Methods

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Abstract: *Electrochemical properties of closo-2,3-dicarbaundecaborane cluster have been investigated potentiostatically using cyclic voltammetry, convolutive voltammetry and galvanostatically via chronopotentiometry techniques combined with digital simulation method at a glassy carbon electrode in 0.1 M tetrabutylammonium perchlorate (TBAP) in solvent dichloromethane. The electroreduction of the carborane cluster exhibited two reduction peaks. The first peak was attributed to a two - electron reduction of carborane to form the dianion. Both the charge transfer processes were followed by fast chemical processes. The second peak represents the further reduction of the dianion by gain one electron to form the trianion followed by a fast chemical reaction. The chemical processes which follow the two - steps of the charge transfer may be due to fast isomerization or structural rearrangement The chemical and electrochemical parameters of the investigated carborane were determined experimentally and verified theoretically via digital simulation method.*

Keywords: Cyclic voltammetry, convolutive voltammetry, dicarbaundecaborane, chronopotentiometry, digital simulation

1. INTRODUCTION

Metallacarboranes derived from the transition metals represent a large family of aromatic borane derivatives which, when combined with a radiometal, is potentially useful in radioimaging and radiotherapy of tumors. The radiometallacarborane may be localized in tumor by a tumor cell-selective antibody molecule to which it is attached or by other means (biomolecule, liposome) [1,2].

One of the interesting properties of carborane clusters is the ability of some of these compounds to undergo thermally induced isomerization [3,4].The polyhedral carboranes can be formally viewed as derived from $B_nH^{2-}_n$ ions by replacement of BH^- groups with isoelectronic and isostructural CH groups. The most symmetric boron cluster species is the divalent anion of *closo*-dodecaborane (Fig. 1a). Its dipotassium salt melts at approximately 810 °C without decomposition [5,6].

The neutral 11-vertex dicarbaborane, 2,3-C2B9H11 (Fig. 1.b) also having 2n+ 2 skeletal electrons and thus also referred to as a closo-polyhedron [7-12].

Morris et al [13]. have analyzed the electrochemical data of simple boron compounds, boranes, metallaboranes, carboranes, and metallacarboranes in view of the formal structural relationship of borane clusters with the number of electron pairs available for bonding. The cyclic voltammetry of BH_3CN^- in acetonitrile [14-18], shows no obvious oxidation or reduction waves at Pt electrode, whereas several reactive electrodes (e.g., Fe, Cu, Co, Ni) led to the formation of metallacyanoborane derivatives. The electrochemical properties of the octahydrotriborate ion, $B_3H_8^-$ in acetonitrile and DMF, underwent one-electron oxidation at a platinum or gold anode to give $B_3H_7.N\text{-}CCH_3$ and $B_3H_7.DMF$ [19] respectively. The reaction was studied chronopotentiometrically and by exhaustive controlled –potential electrolysis. The cyclic voltammogram of $B_{10}H_{12}(NCCH_3)_2$ in CH_3CN at Pt gave two irreversible oxidation peaks at E_p + 0.75 and + 1.2 V($Ag/AgNO_3$) with no well defined corresponding reduction waves [20].

The detection of DNA hybridization with the aid of metallacarborane is of central importance to the diagnosis and treatment of genetic and infectious diseases [21-29].

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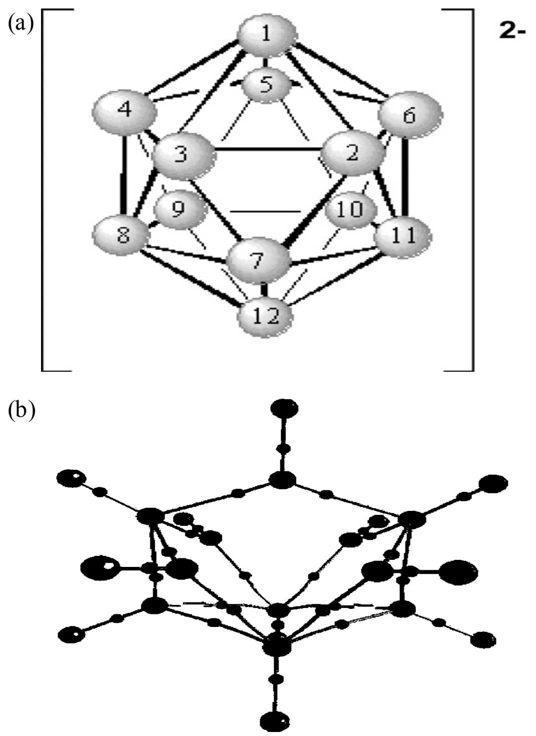


Figure 1. Indicate the structure of the anion of closo-dodecaborane (a) and the Molecular graph of 2,3-C2B9H11 (b).

Metallacarboranes as electrochemical labels are proposed [30]. The electrochemical properties of nucleoside conjugates, derivatives of thymidine (T), 20-deoxycytidine (dC), 20-deoxyadenosine (dA) and 20-deoxyguanosine (dG), containing metalla-carborane complex of cobalt or iron are investigated.

Up to now there have been very few investigations of closo- 2,3-dicarbaundecaborane electrochemistry in CH_2Cl_2, especially via convolutive voltammetry and digital simulation methods [31]. Accordingly, the electrochemical studies, the nature of the electrode reaction, the chemical and the electrochemical parameters of closo-2,3-dicarbaundecaborane (closo-2,3-$C_2B_9H_{11}$) at a glassy carbon electrode in non-aqueous medium have been determined and discussed.

2. EXPERIMENTAL SECTION

2.1. Chemicals

The closo-2,3-dicarbaundecaborane [closo – 2,3 $C_2B_9H_{11}$] was prepared by and obtained from Dr. Kennedy [32] at Leeds University. Standard stock solution of $3x10^{-2}$ M of closo- carborane under investigation was prepared in 0.1M of TBAP in CH_2Cl_2. Tetrabutylammonium perchlorate (TBAP) and CH_2Cl_2 were analytical grade and used as supplied.

2.2. Electrochemical measurements

Cyclic voltammetry, convolution voltammetry and chronopotentiometry experiments were performed using a Princeton Applied Research (PAR) Computer-controlled Potentiostat / Galvanoststic Model 363 (PAR, Oak Ridge, TN, USA). A micro-electrolysis cell with a three electrode system comprising of a glassy carbon electrode (GCE) as the working electrode, a platinum sheet auxiliary electrode and a Ag/$AgNO_3$ in contact with saturated lithium chloride in CH_2Cl_2 / TBAP as a reference electrode was used. Digital simulation of the data for cyclic voltammetric experiments was performed on PC computer using EG & G Condesim software package.

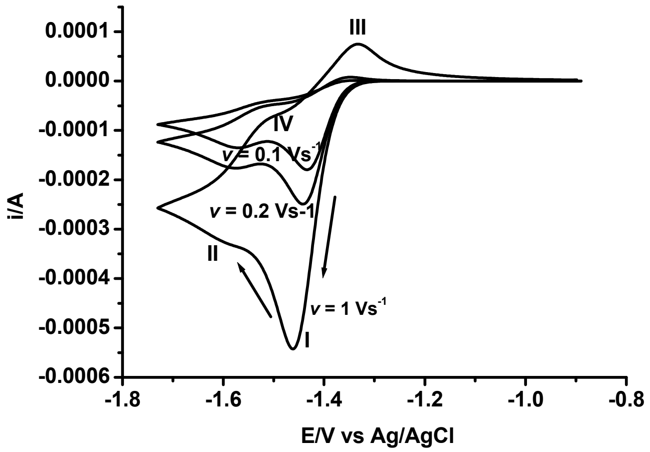


Figure 2. Cyclic voltammogram of closo-2,3 dicarbaundecaborane cluster at a glassy carbon electrode in 0.1M TBAP/CH_2Cl_2 at various value of sweep rate and T = 294 K.

2.3. Procedure

One ml of 3×10^{-2} M solution of closo-2,3 $C_2B_9H_{11}$ was introduced into the electrolysis cell containing 10 ml of 0.1 M tetrabutyl ammonium perchlorate (TBAP) dissolved in methylene chloride. All working solutions were degassed thoroughly with oxygen free nitrogen, and an atmosphere of nitrogen was maintained above the solutions through the course of the experiment. Cyclic voltammetry experiments were performed at temperature ranging from 294 to 234 K.

3. RESULTS AND DISCUSSION

3.1.Cyclic voltammetry study

Cyclic voltammograms of the investigated closo-2,3-dicarbaundecaborane [closo–2,3 $C_2B_9H_{11}$] cluster ware measured in CH_2Cl_2 solvent and 0.1 M TBAP at sweep rates ranging from 0.02–5V/s. Figure 2 gives an example response of the recorded cyclic voltammograms at various sweep rates (0.1 - 1 V/s). As shown the voltammogram exhibited two reduction peaks. The first one (peak I) is unidirection at sweep rate < 1 V/s while the second one (peak II) is coupled with a small anodic peak (IV). This behaviour could be due to the presence of fast chemical steps following both of the charge transfer. It was found that the peak currents increase and the cathodic peak potentials shift to more negative values on increasing the sweep rate. From the cyclic voltammetric investigation, it was found that, the cathodic reduction process is due to the reduction of the carborane cluster via two electrons to give dianion which followed by fast isomerization or structural rearrangement (peak I) while the second peak (II) is due to the reduction of dianion to trianion followed by a chemical step (isomerization or structural

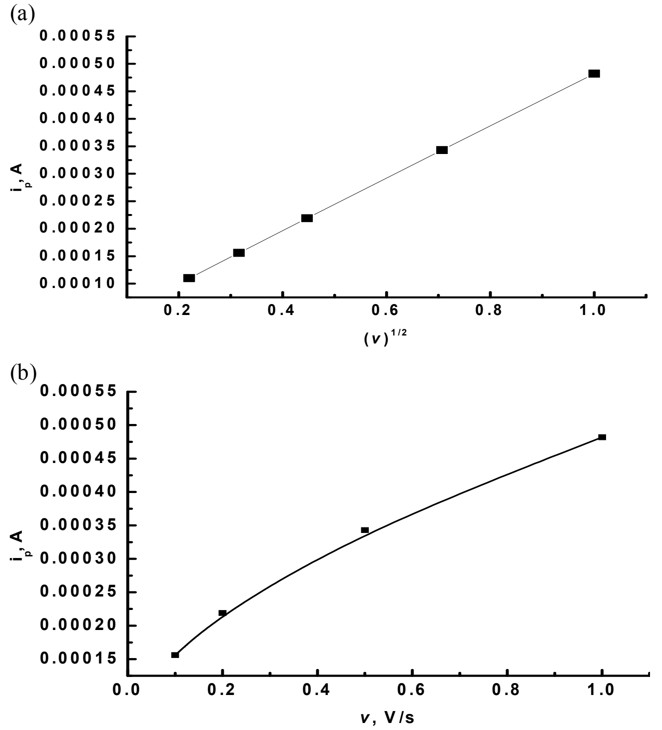


Figure 3. plot of peak current (i_p) of peak I *vs* square root of sweep rate, $(v)^{0.5}$ (a) and *vs* sweep rate (v) (b) of the investigated carborane cluster at T = 294 K.

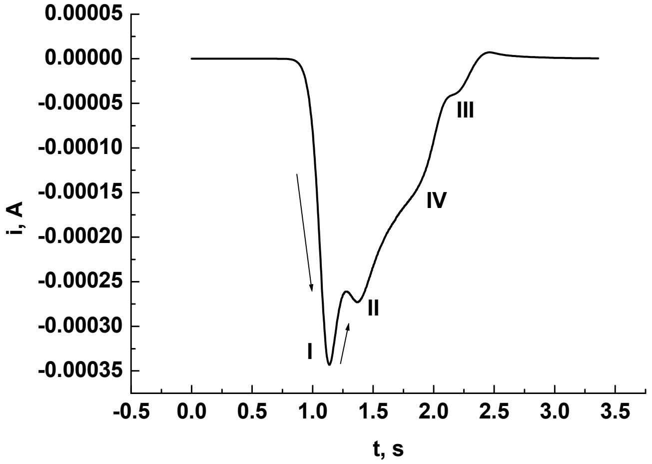


Figure 4. plot of i vs t of the investigated compound derived from cyclic voltammogram at sweep rate of 0.2 Vs^{-1}.

rearrangement) of the investigated closo- carborane cluster.

The reduction peak current of the two reductive peaks, after elimination of the background current, is proportional to the square root, $v^{1/2}$. Also, the measured values of half- peak width (Ep – Ep/2) is more than 56.5/n mV and increase by increasing the sweep rates demonstrate the quasireversibile behaviour of the system, where Ep, Ep/2 and n are the peak potential, the half peak potential and the number of electrons respectively. The influence of potential sweep rate (*v*) on the peak currents, i_p (peak I) in TBAP was studied . Assume that ip α v^x when the electrode process is diffusion controlled, *x* should take a value of 0.5, and for adsorption controlled process it should take a value of 1.0. Fig. 3A indicated that *peak I* increased linearly with increase of $v^{1/2}$,and the corresponding *peak* I – *v* curve tilts (Fig.3B).This confirmed that the diffusion nature of the investigated system at a GCE [33]. From the plot of *i*p vs. √*v*, the diffusion coefficient (*D*) of the electroactive species was determined [33,34]. The calculated values of *D* are cited in Table 1.

The presentation of i vs t of the voltammogram at sweep rate of 0.2 Vs^{-1} is shown in Fig. 4. The plot produce discontinuity Δi_c at t =1.75 s due to the reversibility of the scan. By selecting the data points a cottrel plot is obtained as current versus the reciprocal square root of time. The slope of Cottrel plot yields a diffusion

Table 1. Electrochemical parameters of the investigated closo- 2,3 dicarbaundecaborane cluster**.**

Parameters	Techniques									
	CV		Conv		Decon		CP		Sim	
	a	b	a	b	a	b	a	b	a	b
$k_s \times 10^5$ ms^{-1}	1.900	20.00	-	-	-	-	-	-	1.80	19.80
$E^{o'}$, V	-1.390	-1.550	-	-	-1.392	1.551	-	-	-1.391	-1.552
D × 10^{10}, m^2s^{-1}	7.110	7.210	7.360^c 7.280^d	7.380^c 7.410^d	-	-	7.510	7.310	7.250	7.390
α	-	-	-	-	-	-	-	-	0.49	0.50
$\Delta H^{\neq}$, kJ mol^{-1} (298K)	17.92	19.96	-	-	-	-	-	-	-	-
$\Delta S^{\#}$, $J.K^{-1}.mol^{-1}$ (298K)	-272.4	-280.5	-	-	-	-	-	-	-	-
$\Delta G^{\#}$, kJ mol^{-1}	98.98	103.55	-	-	-	-	-	-	-	-
k_c, s^{-1}	-	-	-	-	-	-	-	-	6	1.2

(a) first wave
(b) second wave
(c) values of the diffusion coefficient (D) via Eq. (4)
(d) values of the diffusion coefficient (D) via Eq. (8)

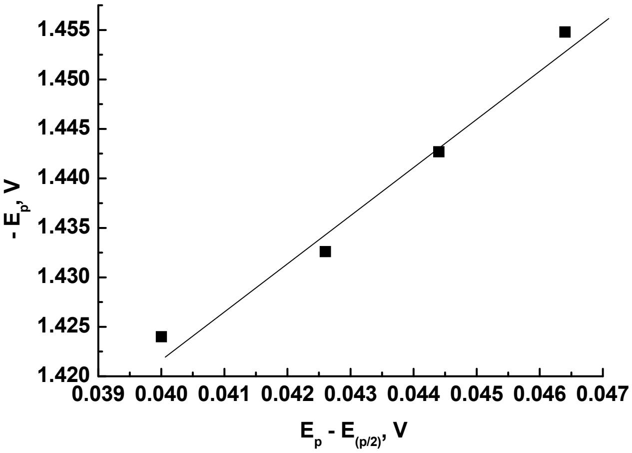


Figure 5. presentation of E_p *vs* E_p - $E_{p/2}$ of the investigated compound at a glassy carbon electrode and T = 294 K.

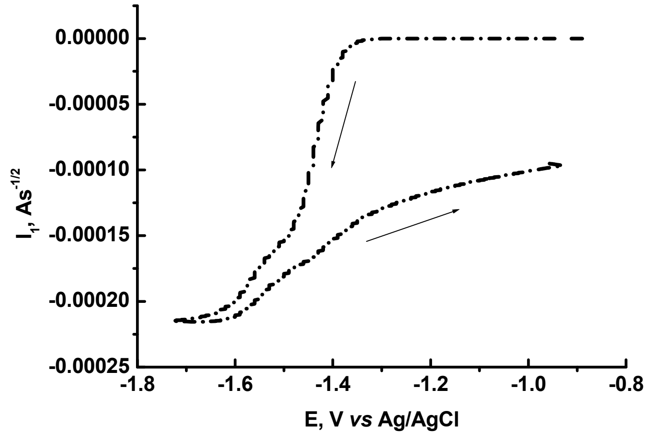


Figure 6. I_1 convolution of closo-2,3 dicarbaundecaborane cluster at sweep rate of 0.2 Vs^{-1}.

coefficient D = 7.2×10^{-10} m^2s^{-1}.

Due to the absence of the anodic peaks at low sweep rates in the backward scan the formal potential ($E^{0'}$) of the first peak of the investigated carborane cluster was calculated from the plot of *E*p vs. (*E*p - *E*p/2) using the following equation [35]:

$$Ep = E^{0'} + (Ep - Ep/2) / Z \tag{1}$$

Where 1/Z is the slope of the plot and Z is defined as $(E_p - E_{p/2}) / (E_p - E^{0'})$. So, from the intercept of this plot (Fig. 5) the value of $E^{0'}$ was determined and listed in Table 1. The standard heterogeneous rates constant ($k_{s1} = 1.9 \times 10^{-5}$ m/s & $k_{s2} = 2.0 \times 10^{-4}$ m/s) were evaluated via the method suggested by Gileadi that does not require the values of peak separation [36,37].

In this case, if E^c_p is plotted against the logarithmic of scan rate, a linear curve at a low scan rate and an ascending curve at a high scan rate are obtained. If both are extrapolated they intersect at a point corresponding to the critical scan rate v_c. The value of k_s is determined via the following equation

$$\log k_s = -0.48\alpha + 0.52 + \log [nF \alpha v_c D_O / 2.303 RT]^{1/2} \tag{2}$$

3.2. Convolutive voltammetry

In cases of straight forward electron transfer or subsequent chemical reaction, the I_1 convolution which is defined [38-48] as:

$$I_1 = (1/\sqrt{\pi}) \int_0^t \frac{i(u)}{\sqrt{t-u}} du \tag{3}$$

allows to determine the diffusion coefficient of the bulk species from the Eq.(4) [34,35]:

$$I_{\lim} = nFAC^b \sqrt{D} \tag{4}$$

where $I_{\lim}$ is the limiting value achieved for I_1 when the potential is driven to a sufficiently extreme value past the wave; the other terms have their usual significance.

The values of the diffusion coefficient (*D*) corresponding to the reduction steps were calculated via Eq. (4) and are listed in Table 1. The I_1 convolution of the investigated closo carborane cluster at a scan rate of 0.2 Vs^{-1} is indicated in Figure 6. The I_1 convolution of the backward sweep display a separation from the forward one and did not return to zero, confirming the sluggishness of the rate of electron transfer and the rapidity of the chemical steps following the charge transfer *i.e* EC_1EC_2 mechanism [35]. Also the forward and backward convolution current produce two waves shape in agreement with the behaviour of the cyclic voltammograms.

The deconvolution of the current (dI_1/d*t*) is defined as [49].

$$ep = (dI_1/dt) = nFAC^b \sqrt{D}\, a\zeta / (1+\zeta)^2 \tag{5}$$

where

$$a = n\nu F/RT \tag{6}$$

and

$$\zeta = \exp [nF/RT (E - E^0)] \tag{7}$$

and the representation of this equation at $v = 0.2$ Vs^{-1} are indicated in Fig. 7. The deconvoluted peak w^p at half-height is equals to 3.53 RT/nF [49] = 90.5 /n mV in case of fast electron transfer. It was found that $w^p > 90.5$ /n mV, which indicating and confirming the moderate fast of charge transfer rate.

The asymmetry and inequality of the forward and reverse sweep of deconvoluted voltammogram, further confirming the quasi-rapidity of charge transfer and the rapidity of the chemical process of closo carborane cluster under consideration [47]. The formal potential was determined from the average peak position of the deconvoluted voltammogram (Table 1). The values of $E^{0'}_1$ & $E^{o'}_2$ determined from deconvoltion voltammgram compare well with the values calculated from cyclic voltammetry (Table 1).

Also, the peak height of deconvoluted current is predicted to proportional to the concentration of the reducible species, to the electrode surface area, and to the sweep rate *v*. The peak shape is very dependent on n (the number of electrons transferred) as n increase, the peak is predicted to become narrower and much higher. Inspection and comparing the cyclic voltammograms and the deconvoluted voltammograms, it was noted that the *(dI_1/dt) vs*

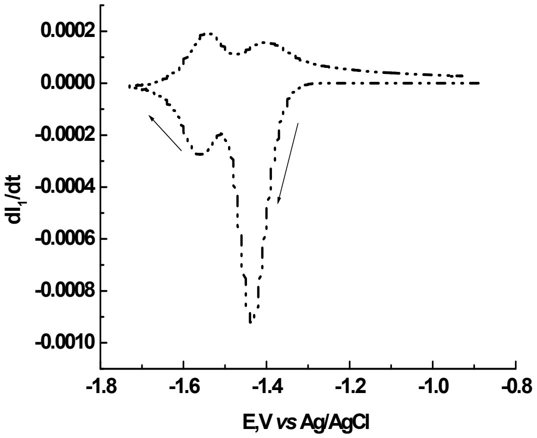


Figure 7. Deconvoluted current of the closo-2,3dicarbaundecaborane cluster at a glassy carbon electrode, sweep rate 0.2 Vs^{-1} and T = 294 K.

E curves were easier to interpret more than *i vs E* curves.

The values of diffusion coefficient were calculated from the deduced convoluted current (I_{limd}) via the following relationship [34,35].

$$I_{\lim d} = \frac{i_p}{3.099\,(\alpha n_a v)^{1/2}} \tag{8}$$

where i_p is the forward peak current and I_{limd} is the deduced limiting convoluted current, which is defined as the limiting convoluted current ($I_{\lim}$) from Eq. (4).The values of diffusion coefficient calculated from Eq. (8) agree well with the value calculated from both cyclic voltammetry and convolutive voltammetry of the experimental voltammogram via Eq. (4) (Table 1).

The number of electrons consumed in electrode reaction was calculated from the following equation [35]:

$$n = 0.0.0864\ ep / \alpha\ v\ I_{\lim} \tag{9}$$

and found to be equal 2 for the first peak and one for the second peak.

From the obtained result, it can be seen that the formal potential of the second reduction process is more negative than that of the first one, which indicates that the activation energy barrier of the second step is higher than that of the first one.

3.3.Chronopotentiometric studies

The chronopotentiometric experiment performed displayed two reduction transitions time (Fig. 8) which agree well with the two reductive voltammetric peaks. The chronopotentiometric transition time was analyzed *via Eq*(10)[50].

$$I_{\lim} = 2i_c(t_s/\pi)^{0.5} = (nFSD^{1/2}C^b) \tag{10}$$

Where i_c is the polarization current, t_s is the transition time of the investigated cluster, and the other symbols have their usual definition. It was found that the values obtained from the chronopotentiometric experiment for the diffusion coefficient was in good agreement with that obtained from *CV* and convolutive voltammetry (Table 1).

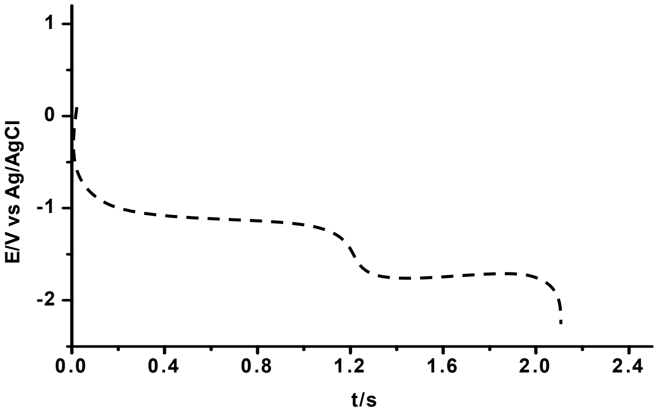


Figure 8. Chronopotentiogram of the closo-2,3dicarbaundecaborane cluster at a glassy carbon electrode and T = 294 K.

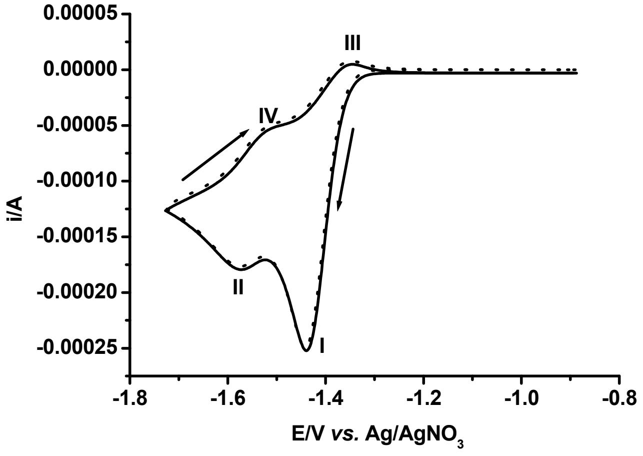


Figure 9. Matching between experimental cyclic voltammogram (- - -) and simulated voltammogram (······) at a sweep rate of 0.2 Vs^{-1} and T =294K.

3.4. Digital simulation

A direct test of the experimental electrochemical parameters was verified via matching of the theoretically generated cyclic voltammograms with the experimental one using the average experimentally determined values of k_s, D and $E^{0'}$, cited in Table 1 for a symmetry coefficient α of 0.49±0.01. The results given in Figure 9 employ the experimental and theoretical values of the electrochemical parameters of the closo-2,3-carborane cluster at sweep rate of 0.2 Vs^{-1} which demonstrate excellent agreement between the captured and the simulated data.

3.5. Effect of temperature on k_s

Eq. (11) gives a simple function of the experimental heterogeneous rate constant with temperature[51].

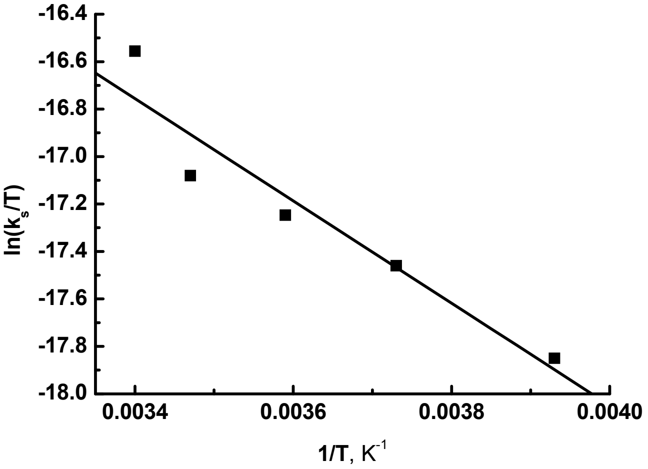


Figure 10. Plot of ln (k_s/T) vs 1/T) of the investigated cluster.

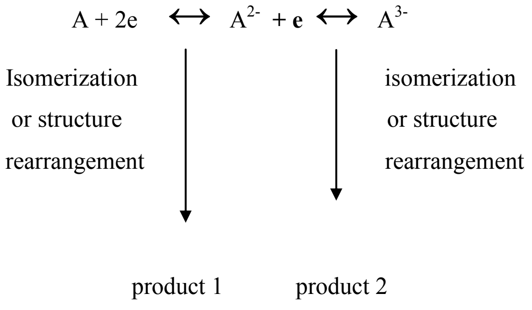
$$In(k_s / T) = In(k / h) - \frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R} \qquad (11)$$

Where k is the Boltzmann constant, h is the Plank constant, R is the gas constant, $\Delta H^{\#}$ is the enthalpy change of activation, $\Delta S^{\#}$ is the entropy change of activation and $\Delta G^{\#}$ is the free energy change of activation. From the plot of ln (k_s/T) vs. 1/T (Fig. 10), $\Delta H^{\#}$ and $\Delta S^{\#}$ was extracted via the slope and the intercept respectively, thus providing $\Delta G^{\#}$ from the following equation:

$$\Delta G^{\#} = \Delta H^{\#} - T\,\Delta S^{\#} \qquad (12)$$

Values of $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ of the investigated cluster are given in Table 1.

Due to the absence of the counter anodic peak coupled with cathodic peak (I) at low sweep rates, the homogeneous chemical rate constant (k_c) was determined via digital simulation. The values of k_c which give best fit between experimental and generating cyclic voltammograms is 6 and 1.2 s^{-1} for the first and the second chemical steps respectively. According to the above discussion the electrode reaction of the investigated closo-2,3-dicarbaundecaborane can be envisaged to proceed as:



4. CONCLUSION

It can be concluded that the electro-reduction of the investigated closo-2,3dicarbaundeca- borane cluster in 0.1 M TBAP/CH_2Cl_2 at a glassy carbon electrode undergo two reduction processes (peaks I & II). The first peak (I) is unidirectional at low sweep rates while, the second peak (II) was coupled with a small anodic peak (IV) The first peak consumed two moderate fast charge transfer followed by a rapid isomerization or structure rearrangement while the second peak consumed one electron with moderate rate of charge transfer followed by a fast chemical step. This behavior demonstrates that the first step of charge transfer produce a dianion and the second step produce a trianion.

The experimental kinetic parameters were determined experimentally and verified theoretically via a digital simulation method by comparing the generated theoretical voltammograms with the experimental voltammograms. The electrode reaction was proposed to proceed as EC_1EC_2.

5. ACKNOWLEDGEMENTS

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