Electrometric studies on the reduction of Ru(III)-EDTA and its hydrazinium complexes

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The electrochemical reduction of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{-} and LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) (where L = ethylenediaminotetraacetate, EDTA; R = Ph or H) has been studied at glassy carbon electrode in a mixture of 0.2 M CH\textsubscript{3}COONa and H\textsubscript{2}SO\textsubscript{4} (pH 2.8) employing cyclic and square wave voltammetry, chronopotentiometry and chronoamperometry methods. The cleavage of N-N bond in the LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) two complexes has been observed at very low potentials caused by the transfer of two electrons from the electrode to the bound hydrazine through metal. The rate constants $k_f$ and $k_l$ for the chemical step associated with the two-electron reduction of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) have been computed from diffusion and catalytic zones, respectively. The standard electron transfer rate constant ($k_{\text{eq}}$) and the electron transfer coefficient ($\alpha$) for the quasi-reversible one-electron reduction of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{-}, have been determined. The diffusion coefficients ($D_{ox}$) for the above complexes have also been reported.

Reduction of metal-bound hydrazine to ammonia is treated as the possible intermediate step in the sequential reduction of dinitrogen catalyzed by bacterial enzyme\textsuperscript{14}. The reaction is assumed to proceed by the transfer of metal electrons together with protons from the surroundings. In an attempt to understand the fundamental nature of the M-N\textsubscript{2} interaction and to develop relatively simple model complexes capable of mimicking the activity of the natural system, numerous transition metal complexes possessing hydrazine or its derivative as a ligand, have been prepared\textsuperscript{5-13} while a few of them have been characterized by structural and spectral studies\textsuperscript{8-13}. The reactivity of some of these compounds with hydridic reagents has been studied\textsuperscript{5,7} and the catalytic ability of very few reducing hydrazines to ammonia and/or amines has been ascertained\textsuperscript{6,11}. Recently, we have successfully investigated\textsuperscript{14,15} the reactions of hydrazine (N\textsubscript{2}H\textsubscript{4})\textsuperscript{2+} and its phenyl derivative (N\textsubscript{2}H\textsubscript{4}Ph\textsuperscript{+})\textsuperscript{15} with Ru(III)-EDTA complexes which gave two monomer complexes by spectrophotometry and voltammetry. We further demonstrated\textsuperscript{14-16} the excellent property of ruthenium pumping electrons with ease from the source (Hg-electrode between the potentials +0.1 to -0.5 V vs SCE) to N-N bonds so as to cleave heterolytically in subsequent steps. The present study on the electrochemical reduction of hydrazinium (N\textsubscript{2}H\textsubscript{4})\textsuperscript{2+} and phenylhydrazinium (N\textsubscript{2}H\textsubscript{4}Ph\textsuperscript{+}) complexes of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{-} at more effective pH 2.8 at a glassy carbon electrode was carried out for a better incisive into the chemical steps following the two-electron reduction of ruthenium, employing cyclic voltammetry, chronopotentiometry, chronoamperometry and square wave voltammetry.

Materials and Methods

The compound K[Lu\textsuperscript{III}(HL)Cl].2H\textsubscript{2}O used to obtain LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{-} in aqueous solution, was prepared from RuCl\textsubscript{3}.xH\textsubscript{2}O via K\textsubscript{2}[RuCl\textsubscript{5}(OH\textsubscript{2})] and it was characterized by the procedures described earlier\textsuperscript{17}. N\textsubscript{2}H\textsubscript{4}HSO\textsubscript{4} (BDH), N\textsubscript{2}H\textsubscript{4}PhCl (Allied Chemicals, USA) and CH\textsubscript{3}COONa (SD Fine Chemicals) were used without further purification. A mixture of 0.2 M CH\textsubscript{3}COONa and H\textsubscript{2}SO\textsubscript{4} (pH 2.8) served as the supporting electrolyte.

Cyclic (CV) and square wave (SWV) voltammograms, chronopotentiograms (CP) and chronoamperograms (CA) were recorded with EG & G PARC model 273A Potentiostat/Galvanostat coupled with a three electrode cell assembly and Gateway 2000 (4DX2-66) computer. A glassy carbon of 0.0314 cm\textsuperscript{2} area was used as working electrode and its potentials were measured with reference to Ag/AgCl (0.222 V vs NHE) in 3 M NaCl. The platinum wire separated from the anal-
ytical solution by a vycor tip bridge, served as a counter electrode. The EG & G model 271 Cool Kinetics software was used to deduce the requisite kinetic parameters.

LRuIII(N2H4R) under investigation was prepared in situ by mixing LRUIII(OH2) (2 mM) and N2H5HSO4/N2H4PhCl in 1:100 molar ratio to maintain pseudo order conditions in 10 ml of supporting electrolyte. Prior to recording the data, each set of the above experimental solutions was degassed with Ar.

Values of the transfer coefficient (α) and the standard rate constant (k′) corresponding to quasi-reversible one-electron reduction of LRUIII(OH2) were obtained by constructing suitable theoretical CV and SWV voltammograms and comparing them with the experimental curves. Similarly, the rate constants k′, k and k′, for the coupled chemical steps associated with the two-electron reduction of LRUIII(N2H4R) were computed from diffusion (0.5-1.5 V s⁻¹ in CV and 50-1500 Hz in SWV) and catalytic (0.005-0.1 V s⁻¹ in CV and 2-10 Hz in SWV) zones, respectively. The Dms data for LRUIII(OH2) and LRUIII(N2H4R) were derived from CP and CA based on the first electrochemical reduction step.

Results and Discussion

Voltammetry

Complexes LRUIII(OH2) and LRUIII(N2H4R) were studied by CV at 0.01 to 60 V s⁻¹ scan speed and SWV at 1 to 500 Hz frequency in the potential range of +0.2 to -0.8 V. They exhibited well-defined voltammograms. Representative cyclic and square wave voltammograms are illustrated in Figs 1 and 2 and the important CV data are presented in Table 1. At 0.05 V s⁻¹ scan, LRUIII(OH2) exhibited a pair of cathodic at -0.222 V and anodic at -0.139 V peaks in CV (Fig. 1a) representing the Ru(III)/Ru(II) couple. The ratio of anodic to cathodic peak height was less than one, however, its height increased with

<table>
<thead>
<tr>
<th>Complex</th>
<th>Scan speed (V s⁻¹)</th>
<th>Ru(III)/Ru(II)</th>
<th>Ru(III)/Ru(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRUIII(OH2)</td>
<td>0.05</td>
<td>0.222</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.224</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.237</td>
<td>0.124</td>
</tr>
<tr>
<td>LRUIII(N2H5)</td>
<td>0.05</td>
<td>0.220</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.222</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.239</td>
<td>0.126</td>
</tr>
<tr>
<td>LRUIII(N2H4Ph)</td>
<td>0.05</td>
<td>0.463</td>
<td>0.444</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.518</td>
<td>0.458</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.563</td>
<td>0.502</td>
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the increase in the square root of scan speed ($\sqrt{v}$). The $i_p/\sqrt{vC}$ value for cathodic peak was 17.13 at 0.1 V s\(^{-1}\) and almost constant at other scan speeds as illustrated in Table 1, establishing the electrode process to the diffusion controlled. Both peaks took broad shape as the scan speed increased. Besides, the cathodic peak shifted to more negative potentials while anodic peak to anodic potentials thus increasing the peak to peak separation ($\Delta E_p$) from 83 mV (0.05 Vs\(^{-1}\)) to 226 mV (5 Vs\(^{-1}\)). Further, the difference in $E_p$ and $E_{p2}$ values (Table 1) increased beyond 80 mV. In SWV, LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} exhibited a single cathodic peak at $-0.185$ V at 10 Hz (Fig. 2a) which gradually shifts to $-0.151$ V as frequency approaches 400 Hz, with a concomitant increase in the peak width at half peak height, from 149 mV to 201 mV. These characteristic features are consistent with the quasi-reversibility of Ru(III)/Ru(II) couple\textsuperscript{14}.

LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) displayed two cathodic waves at $-0.068$ V and $-0.220$ V (Fig. 1b) in the forward CV scan at 0.05 V s\(^{-1}\). Heights of these responses correspondingly increased with the inward CV scan at 0.05 V s\(^{-1}\). Heights of these responses were relatively 260-280 mV more negative than those of LRU\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) which may be the anodic counterpart of the peak at $-0.068$ V, thus, confirming its microscopic reversibility. Absence of this anodic peak at other scan speeds is therefore accounted for the fast decomposition of the reduced product at $-0.068$ V. Then, one-electron reduction of the decomposed product at $-0.220$ V is the next step. Accordingly, LRU\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) showed two SWV reduction peaks at $-0.009$ V and $-0.178$ V (Fig. 2b).

Two cathodic responses at $-0.326$ and $-0.499$ V in the forward and no response in the reverse scan were observed in CV (Fig. 1c) for LRU\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph) at 0.05 V s\(^{-1}\). The anodic response did not exhibit much change when the scan speed was raised to 60 V s\(^{-1}\) or when the potential was switched at the foot of the second wave, thus indicating irreversible nature of two reduction steps. The measured potentials of both responses were relatively 260-280 mV more negative than those of LRU\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) which may be the direct result of phenyl group substitution on the coordinated N of hydrazine. The data given in Table 1 indicated a cathodic shift in peak position of both these cathodic responses and a proportionate increase in peak intensity with the increase in $\sqrt{v}$ value. However, plots of $i_p$ against $\sqrt{v}$ confirmed the overlap of catalytic currents with the diffusion currents at $v<0.1$ V s\(^{-1}\) as found in the case of LRU\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4})\textsuperscript{14}. Examination of $E_p$ and $E_{p2}$ values (Table 1) showed these steps as one-electron process. But, the measured $i_p/\sqrt{vC}$ value for the first peak was nearly double the value of the second peak which in turn strongly confirmed the involvement of two electrons in the first reduction process. Surprisingly, complex LRU\textsuperscript{II}(N\textsubscript{2}H\textsubscript{4}Ph) under similar experimental conditions exhibited distinct results at Hg-electrode\textsuperscript{15}. It depicted three cathodic peaks ($-0.157$, $-0.270$, and $-0.456$ V vs SCE), of which the middle one was less intensive at hanging mercury drop electrode (HMDE). The responses at $-0.157$ and $-0.270$ V exhibited their anodic counterpart at $v>0.1$ V s\(^{-1}\). Based on the analysis data, the first step was assigned for the reduction of LRU\textsuperscript{II}(N\textsubscript{2}H\textsubscript{4}Ph) to LRU\textsuperscript{II}(NH\textsubscript{2}Ph)\textsuperscript{2−}. The latter being highly unstable in the solution decomposed to LRU\textsuperscript{II}(NH\textsubscript{2}Ph)\textsuperscript{−} and one mole of NH\textsubscript{3}. Finally, the reduction steps at $-0.254$ V and $-0.417$ V were assigned respectively for the partially hydrolyzed and un-hydrolyzed complexes of

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Fig. 3—Cyclic voltammogram of LRU\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) (2 mM) at scan speeds (a) 1, (b) 3 and (c) 40 V s\(^{-1}\)
LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph)\textsuperscript{−}. Comparison with the present data in Fig. 1c showed that the LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4})\textsuperscript{2−} species is more labile at glassy carbon electrode than at HMDE. The complex LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph) once again showed two reduction peaks instead of three in SWV as seen in Fig. 2(c).

The chronoamperograms of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} and LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) at potentials beyond their reduction peaks, first peak in the latter complexes, are well-defined. In each case, the plot of \(i\) vs \(t\) was linear and followed ideal Cottrell’s behaviour indicating that the reduction process is diffusion controlled. Slope of these plots was employed to calculate \(D_{\alpha}\).

Potential-time plots for LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} and LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) were obtained by applying current densities ranging between 0.08 and 0.5 \(\mu\)A/cm\textsuperscript{2}. Some of the typical \(E-t\) plots are depicted in Fig. 3 (a-c). A single chronopotentiometric step for LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} (Fig. 3a) and two for LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) (Figs 3 b, c) were observed. The values of transition time (\(\tau\)) were in the range 2.2 to 4.8 s in case of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} and 1.8 to 7.3 s for Ru(III)/Ru(I) step and 37.35 and 24.58 s for Ru(III)/Ru(II) in case of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R). The \(i\)-\(t\) values for Ru(III)/Ru(I) and 8.28 to 37.4 s for Ru(III)/Ru(II) in case of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R). The \(i\)-\(t\) values in each case were fairly constant. The measured \(\tau\) values at 6 \(\mu\)A were found to be 7.29 and 3.93 s for Ru(III)/Ru(I) step and 24.58 s for Ru(III)/Ru(I) couple in LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) and LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph) complexes, respectively. The trend, same at other current densities also indicates that the \(\tau\) values for Ru(III)/Ru(I) couple in LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph) is almost half of the value of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) but both the values were much less as compared to the value of their respective succeeding Ru(III)/Ru(II) step (Fig. 4). These observed trends may be due to chemical complications associated with the reduction processes. The plot of \(i\) vs \(\tau\) in each case, was linear (Fig. 4 B) which has confirmed the nature of electrode reaction as diffusion controlled. With the help of this data, the values of \(D_{\alpha}\) were evaluated using the equation given by Sand\textsuperscript{18}.

**Mechanism of electroreduction of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R)**

The constant potential electrolysis data of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) at Ru(III)/Ru(I) potentials as reported earlier\textsuperscript{14,15} revealed the constant reduction of hydrazines to ammonia and/or aniline. Therefore, the reduction mechanism of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) can be composed of following electrochemical and chemical reactions (1-4).

\[\text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{R}) + 2e^- \rightarrow \text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{AR})^{2-} \quad \ldots (1)\]

\[\text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{R})^{2-} \rightarrow \text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{R})^{2-} + \text{NH}_3 \quad \ldots (2)\]

\[\text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{R})^{2-} + \text{H}^+ \rightarrow \text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{R})^{2-} + \text{NH}_2\text{R} \quad \ldots (3)\]

\[\text{LRu}^{\text{III}}(\text{NH}_2\text{R})^{2-} + e^- \rightarrow \text{LRu}^{\text{III}}(\text{NH}_2\text{R})^{2-} \quad \ldots (4)\]

**Kinetic parameters**

The estimated values of kinetic parameters \(\alpha, k_i, k_f, k_r\) and \(D_{\alpha}\) pertaining to one-electron reduction of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} and two-electron reductions of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}R) species are compiled in Table 2. The values of \(\alpha\) and \(k_i\) in Table 2 obt-

**Table 2—Kinetic parameters for the one-electron reduction of LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−} and two-electron reduction of LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}) and LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph) in 0.2 \(M\) CH\textsubscript{3}COONa-H\textsubscript{2}SO\textsubscript{4} mixture at 25°C, pH 2.8**

<table>
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<tr>
<th>Complex</th>
<th>(\alpha)</th>
<th>(k_i\times 10^3) (cm\textsuperscript{s}\textsuperscript{−}1)</th>
<th>(D_{\alpha}\times 10^8) (cm\textsuperscript{s}\textsuperscript{−}1)</th>
<th>(k_f\times 10^3) (cm\textsuperscript{s}\textsuperscript{−}1)</th>
<th>(k_r\times 10^3) (cm\textsuperscript{s}\textsuperscript{−}1)</th>
<th>(k_r) (M\textsuperscript{−}1\textsuperscript{s}\textsuperscript{−}1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRu\textsuperscript{III}(OH\textsubscript{2})\textsuperscript{−}</td>
<td>0.36</td>
<td>0.33</td>
<td>5.97</td>
<td>5.47</td>
<td>7.11</td>
<td>8.28</td>
</tr>
<tr>
<td>LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4})</td>
<td>—</td>
<td>—</td>
<td>4.68</td>
<td>5.73</td>
<td>1.73</td>
<td>2.62</td>
</tr>
<tr>
<td>LRu\textsuperscript{III}(N\textsubscript{2}H\textsubscript{4}Ph)</td>
<td>—</td>
<td>—</td>
<td>5.45</td>
<td>4.33</td>
<td>3.87</td>
<td>4.57</td>
</tr>
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</table>
tained for \( \text{LRu}^{\text{III}}(\text{OH}_2)^- \) by CV were in consonance with those obtained by SWV. Similarly, the value of \( D_{ox} \) obtained for this species from CA and CP data were nearly equal and in conformity with the value, \( 6 \times 10^{-6} \text{ cm}^2\text{s}^{-1} \) derived polarographically at pH 3.68.

Values of \( k'_j \) and \( k''_j \) (Table 2) obtained from CV data for both the hydrazine complexes were in good agreement with those derived from SWV data. However, the salient features in \( k'_j \) and \( k''_j \) values were that the value of \( k'_j \) was nearly thousand times greater than that of \( k''_j \) of the same complex and the value of \( k'_j \) decreased while maintaining the \( k''_j \) value same on the introduction of phenyl group on the bound N of hydrazine ligand. Based on these trends, it is predicted that reaction (2) was much faster than reaction (4). The catalytic ability of ruthenium metal in the present systems apparently depend on both the chemical steps (reactions 2 and 4). While, the steric repulsion and hydrophobic nature caused by the phenyl ring in \( \text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{Ph}) \) on the bound N of hydrazine ligand. The catalytic ability of ruthenium metal in the present systems apparently depend on both the chemical steps (reactions 2 and 4). While, the steric repulsion and hydrophobic nature caused by the phenyl ring in \( \text{LRu}^{\text{III}}(\text{N}_2\text{H}_4\text{Ph}) \) on the bound N of hydrazine ligand. From the \( k''_j \) values of two hydrazinium complexes, it could be concluded that the phenyl substitution on the N of the incoming hydrazine has less influence on the lability of \( \text{LRu}^{\text{III}}(\text{NH}_2\text{R})^- \) species.

Acknowledgement

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References