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Interaction of phenylhydrazine with Ru^{III}–EDTA complexes: reduction of phenylhydrazine to ammonia and aniline in aqueous acidic conditions

Raju Prakash, Beena Tyagi, Debabrata Chatterjee and
Gadde Ramachandraiah*

Reactive Polymers and Catalysis Divisions, Central Salt and Marine Chemicals Research Institute,
Bhavnagar-364002, India

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Abstract—Reaction of the phenylhydrazinium ($PhN_2H_4^+$) ion with the labile aquo complexes of $[Ru^{III}(HEDTA)(H_2O)]$ (EDTA = ethylenediaminetetraacetate) was studied electrochemically employing sampled DC, cyclic voltammetry and differential pulse techniques in 0.2 M CH_3COONa and H_2SO_4 mixture between pH 1.0 and 4.5 at 25°C. It produced two phenylhydrazinium complexes, namely $[Ru^{III}(HEDTA)(N_2H_4Ph)]^+$ and $[Ru^{III}(EDTA)(N_2H_4Ph)]$ in the rapid aquo-substitution reactions. The second-order rate constants, k_1, for the formation of the former, and k_2 for the latter are 0.98 and 36.85 M^{-1} s^{-1}, respectively, as determined spectrophotometrically by following the intensity of the LMCT band at 420 nm. The complex, $[Ru^{III}(HEDTA)(N_2H_4Ph)]Cl \cdot 2H_2O$ was prepared and characterised by physicochemical methods. These phenlhydrazinium complexes were reduced by two electrons at $E_{1/2} = -0.175$ V *vs* SCE, producing one mole of NH_3 and the corresponding Ru^{III}–NH_2Ph complexes in subsequent rapid decomposition steps. The unstable Ru^{III}–NH_2Ph complexes were rapidly hydrolysed to one mole of NH_2Ph and the respective aquo complex. One-electron reduction steps for the regenerated aquo complex at ($E_{1/2}$) -0.254 V and the unhydrolysed Ru^{III}–NH_2Ph complex at -0.417 V were also observed. Phenylhydrazine was reduced to ammonia and aniline by constant potential coulometry at -0.200 V(Hg) *vs* SCE, in the presence of $[Ru^{III}(HEDTA)(H_2O)]$ at 100 : 1 molar ratio. The turnover number (per mole of catalyst per hour) with respect to ammonia is 5.98 and 2.82 at pH 2.8 and 1.9, respectively. The probable mechanisms for the electroreduction of the above phenylhydrazinium complexes and the catalytic reduction of phenylhydrazine to NH_3 and NH_2Ph, are proposed. Copyright © 1997 Elsevier Science Ltd

Keywords: Ru^{III}–EDTA; phenylhydrazine; interaction; electrocatalysis; ammonia; aniline

We have studied the chemistry of Ru–EDTA complexes extensively [1–7] and the present work is a continuation of our efforts to develop a simple water-soluble metal complex for activating and reducing the N—N bonded molecules to ammonia and/or amines in order to elucidate the pathways for N—N bond reductions in homogeneous solution. Metal bound hydrazine is considered to be the active intermediate in nitrogen fixation by primitive organisms, e.g. *Azotobacter*, carrying a nitrogenase system [8–11]. Our earlier communications [8,12,13], revealed the reduction of hydrazinium [12] and azide [13] ions, surprisingly, at unexpected potentials of the Hg electrode catalysed by Ru–EDTA complexes in aqueous acidic conditions. To obtain more mechanistic details and to study the substitutional effect on the coordinated N of hydrazine in this intriguing N—N bond reduction, we have selected phenylhydrazine as a substrate in the present study. The results of spectrophotometric, kinetic and electrochemical studies of the interaction of phenylhydrazine with Ru^{III}–EDTA complexes in aqueous acidic solutions are reported. The results are correlated with the data reported for hydrazinium and azide ions.

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* Author to whom correspondence should be addressed.

EXPERIMENTAL

Materials

$K[Ru^{III}(HEDTA)Cl] \cdot 2H_2O$ was prepared from $K_2[Ru^{III}Cl_5(H_2O)]$ by previously reported methods, and was characterised [14,15]. This complex, as evidenced earlier [12,16] by spectrophotometric and kinetic data, quickly changes to $[Ru^{III}(HEDTA)(H_2O)]$ ($pK_a = 2.37$) in aqueous solution of pH 1.0–4.5. Hence, $[Ru^{III}(HEDTA)(H_2O)]$ has been considered as the precursor in this study. Phenylhydrazine hydrochloride (N_2H_4PhCl) was obtained from Allied Chemicals, U.S.A. and used as a source for $N_2H_4Ph^+$ ion. All other chemicals used were of AR grade.

$[Ru^{III}(HEDTA)(N_2H_4Ph)]Cl \cdot 2H_2O$ was prepared by dissolving $K[Ru^{III}(HEDTA)Cl] \cdot 2H_2O$ (100 mg, 0.2 mmol) phenylhydrazine hydrochloride (30.66 mg, 0.21 mmol) in the minimum quantity of water. The resulting dark yellow solution was stirred for 2 h at 45° under Ar atmosphere. The product was precipitated with absolute alcohol, filtered and washed repeatedly with 9 : 1 acetone–water mixture and dried *in vacuo*. Found: C, 33.7; H, 4.4; N, 9.8. Calc. for $[Ru^{III}(HEDTA)(N_2H_4Ph)]Cl \cdot 2H_2O$: 33.5; H, 4.1; N, 9.4%. IR (cm^{-1}): 3210 (N—H stretching), 1750 (COOH), 1640 (coordinated COO^-), 1420 and 1080 (N—H deformations).

pH-metric titrations

N_2H_4PhCl was titrated with standard NaOH (0.1 M) solution as usual [14] and from the resulting pH data, the acid dissociation constant (pK_a) of $NHPh \cdot NH_3^+$ ion was calculated as 5.15 ± 0.01 at 25°C. Similar titrations were carried out with $[Ru^{III}(HEDTA)(H_2O)]$, in the absence and presence of one equivalent of N_2H_4PhCl. This data revealed that the acidic proton on the more basic nitrogen in $NHPh.NH_3^+$ is unaffected during its interaction with the Ru^{III} centre. This is sufficient to prove the coordination of $N_2H_4Ph^+$ at the sixth vacant position on Ru^{III} through its weak basic NHPh group.

Measurements and method

Electrochemical measurements such as sampled DC, differential pulse polarography (DPP), cyclic voltammetry (CV) and differential pulse voltammetry (DPV), were performed with EG&G Princeton Applied Research models: 174A polarographic analyzer, 175 universal programmer with a high-precision *X–Y* recorder. A three-electrode assembly of EG&G PAR model 303, comprising a Pt wire auxiliary, SCE reference and a dropping mercury electrode (DME) of 3.85 mg s^{-1} or a hanging mercury drop electrode (HMDE) of 0.021 cm^2 was used. All *E–i* plots were recorded under Ar in the potential range +0.2 to −0.8 V. The electrochemical cell was thermostatted to 25°C within ±0.1°C. Controlled potential coulometry (CPC) was carried out using a EG&G PAR model 173 galvanostat and 179 digital integrator in a three-compartment cell. The auxiliary Pt mesh and the reference SCE electrodes were separated from the main compartment cell by fine (G4) glass frits. The main compartment contained Hg-pool (1-inch convex surface diameter) as the working electrode with a glass disk agitator just above the mercury surface. A 30-ml solution containing 0.2 M CH_3COONa, 30 μmol $K[Ru^{III}(HEDTA)Cl] \cdot 2H_2O$ and 30 mmol N_2H_4PhCl, having the pH adjusted to the required value (1.9 or 2.8) with H_2SO_4 solution, was electrolysed for 10 h at −0.200 V under Ar. The quantity of ammonia produced was estimated at 1 h intervals using an Orion 940 ion analyser equipped with an ammonia-sensing electrode [12]. Aniline, produced along with ammonia, was tested using vanadium(V) salt [17].

The electronic absorption spectra were recorded at 25°C using a Shimadzu UV–vis NIR scanning spectrophotometer, model UV-3101 PC. Kinetic studies were carried out on a Hi-Tech stopped-flow spectrophotometer, SF-51 coupled to an Apple data processor. The observed rate data for the formation of the phenylhydrazinium complex were obtained by monitoring absorbance changes in the growth of the characteristic LMCT band at 420 nm. Experiments were conducted under pseudo-first-order conditions of excess phenylhydrazine hydrochloride concentration. The ionic strength of the kinetic solution was adjusted with 2 M KCl. The temperature was maintained to 25±0.1°C using a built-in thermostatic cell compartment.

RESULTS AND DISCUSSION

Voltammetry

The *E–i* responses of $[Ru^{III}(HEDTA)(H_2O)]$ species in the absence and presence of one equiv. N_2H_4PhCl at pH 2.8 were examined at the DME (sampled DC, DPP) and the HMDE (CV and DPV). In the absence of N_2H_4PhCl, the complex exhibited a cathodic wave at $E_{1/2} = -0.213$ V in sampled DC and a pair of cathodic (−0.236 V) and anodic (−0.173 V) peaks in CV, which conforms with the reported values assigned for the $Ru^{III/II}$ couple [12,13].

In the presence of N_2H_4PhCl, after 3–5 min of equilibration, $[Ru^{III}(HEDTA)(H_2O)]$ showed three closely separated reduction waves in sampled DC (Fig. 1a) at $E_{1/2} = -0.155$, −0.233 and −0.407 V. The overall wave height at −0.5 V is nearly three and a half times larger than that of the $[Ru^{III}(HEDTA)(H_2O)]$ one-electron wave. These changes are accounted for by the formation and subsequent participation of phenylhydrazinium complexes in the electrochemical processes. The $E_{1/4} - E_{3/4}$ values of these waves were measured as 30, 55 and 60 mV which indicated the first wave as a two-electron process and

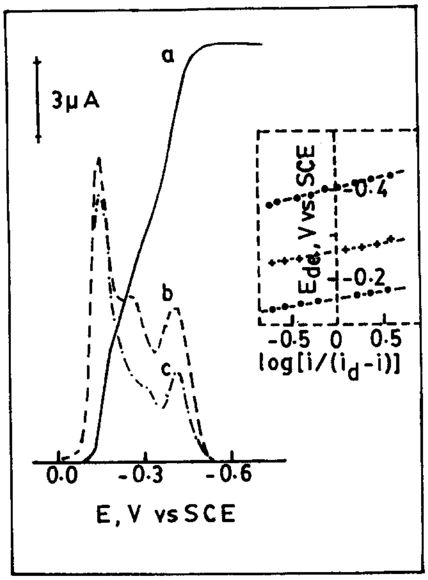


Fig. 1. Voltammetric responses of $[Ru^{III}(HEDTA)(H_2O)]$ (1 mM) in the presence 1 equiv. of N_2H_4PhCl. (a) Sample DC, (b) DPP, (c) DPV. pH = 2.8. Inset: Plots of E_{de} *vs* log $\{i/(i_d-i)\}$ for the polarographic steps shown in (a).

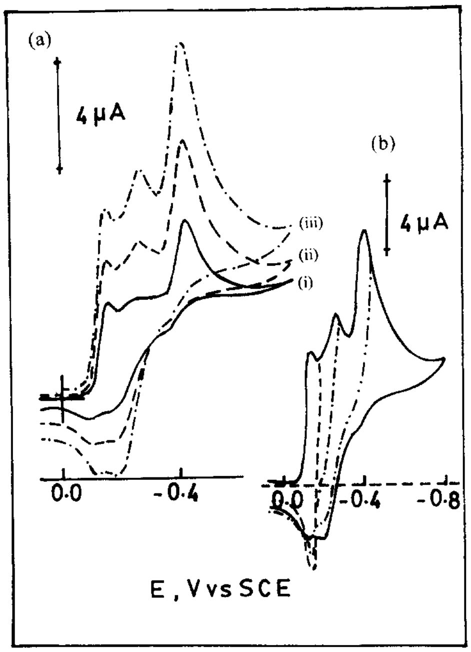


Fig. 2. Cyclic voltammograms of $[Ru^{III}(HEDTA)(H_2O)]$ (1 mM) in the presence of 1 equiv. N_2H_4PhCl at the potential scan speed (a) (i) 0.02, (ii) 0.05, (iii) 0.1 V s^{-1} and (b) 0.1 V s^{-1} at various switching potentials.

the last two as one-electron processes. The plots of E_{de} *vs* log $i(i_d-i)$ were linear as seen in the inset of Fig. 1 indicating that all three waves in Fig. 1a are diffusion controlled and reversible at the DME.

The behaviour of $[Ru^{III}(HEDTA)(H_2O)]$ in the presence of 0.1–100 equiv. N_2H_4PhCl was also studied. The diffusion current at −0.5 V had increased linearly with the concentration of N_2H_4PhCl between 0.1–1.0 equivalent, whereas the changes in the overall total diffusion current and the $E_{1/2}$ values at higher equivalents of N_2H_4PhCl were inconspicuous. However, the height of the second wave had reached a minimum value at $[N_2H_4PhCl]/[Ru^{III}(HEDTA)(H_2O)] \geqslant 10$. A plot of the mole ratio of N_2H_4PhCl to the complex against the diffusion current at −0.5 V suggested the formation of monomeric phenylhydrazinium adducts; namely $[Ru^{III}(HEDTA)(N_2H_4Ph)]^+$ and $[Ru^{III}(EDTA)(N_2H_4Ph)]$, as was confirmed spectrophotometrically.

Figure 1 (b and c) shows the DPP and DPV responses of the above solution. While the position of these peaks correlated with the $E_{1/2}$ values of the corresponding waves in Fig. 1a, the second peak diminished and moved to cathodic potentials in DPV. Whilst, in CV, three cathodic peaks at −0.157, −0.270 and −0.456 V in the forward scan, and two anodic peaks at −0.118 and −0.185 V (counterparts of the first two) in the reverse scan (Fig. 2a), were observed. There was no anodic counterpart to the third cathodic response. Peak intensities of all three cathodic (CV) responses varied as a function of the square root of the scan speed, while peak positions remained static. Although, the two anodic peaks appeared closely separated at scan speeds <0.1 V s^{-1} (see Fig. 2a, part ii) or the potentials were switched to the foot of the second/third cathodic waves (see Fig. 2b), they diminished slowly as the scan approached 0.02 V s^{-1}.

The effect of pH on the $E_{1/2}$ of the waves in Fig. 1a, and the difference in diffusion current at −0.5 V in the absence and presence of 1 and 100 equiv. of N_2H_4PhCl, were measured. The half-wave potential of the waves in Fig. 1(a) was not shifted significantly. However, the enhanced current at −0.5 V changed considerably, as shown in Fig. 3. The rise in the diffusion current was a maximum in the pH range 2.0–3.5. The lowering of enhanced diffusion current between pH 1.0 and 2.0 is the result of the low rate of formation of $[Ru^{III}(HEDTA)(N_2H_4Ph)]^+$, while that at pH > 3.5 is owing to the stabilization of the $[Ru^{III}(EDTA)(N_2H_4Ph)]$ complex.

Spectrophotometry

The reaction of $[Ru^{III}(HEDTA)(H_2O)]$ with N_2H_4PhCl in 0.2 M CH_3COONa and H_2SO_4 mixture (pH 2.8) accompanied the spectral change producing a new absorption (ligand to metal charge transfer) band at 420 nm. Spectral changes that occurred immediately after the addition of N_2H_4PhCl to a solution of $[Ru^{III}(HEDTA)(H_2O)]$ in different molar ratio at pH 2.8 are shown in Fig. 4a. The kinetics of the reaction were studied as a function of $[N_2H_4PhCl]$ and pH under pseudo-first-order conditions at 25°C. The values of observed rate constant of formation (k_{obs})

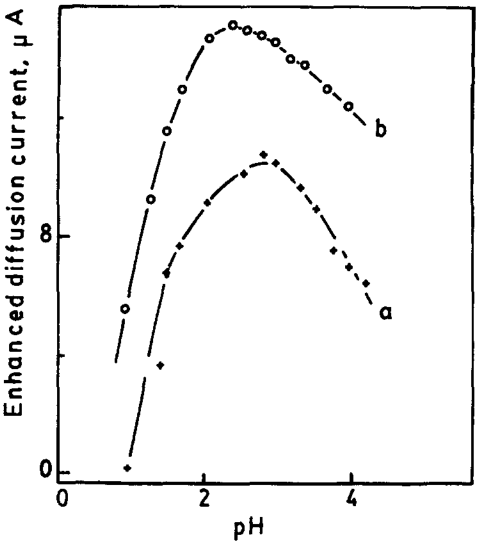


Fig. 3. Influence of solution pH on the enhanced diffusion current (Δi_d) at -0.45 V in the presence of (a) 1, (b) 100 equiv. of phenylhydraine. [$\mathrm{Ru^{III}(HEDTA)(H_2O)}$], 1 mM.

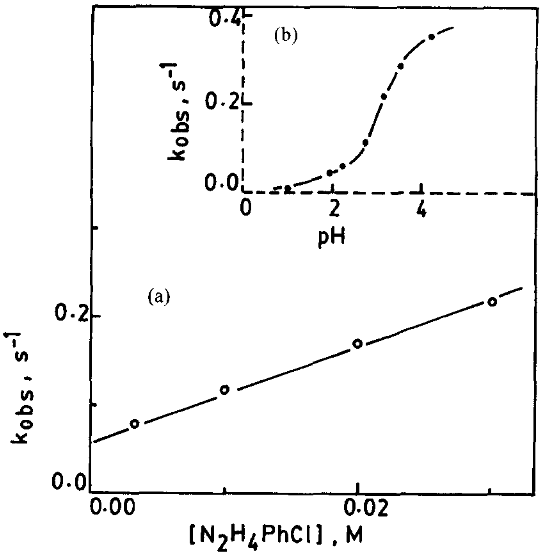


Fig. 5. (a) Plot of k_{obs} *vs* [$\mathrm{N_2H_4PhCl}$]. [$\mathrm{Ru^{III}(HEDTA)(H_2O)}$], 0.5 mM, pH 2.8. (b) Plot of k_{obs} *vs* pH: [$\mathrm{Ru^{III}(HEDTA)(H_2O)}$], 0.5 mM; [$\mathrm{N_2H_4PhCl}$], 0.02 M.

of the hydrazinium adduct changed linearly with [$\mathrm{N_2H_4PhCl}$]. The plot of k_{obs} *vs* [$\mathrm{N_2H_4PhCl}$] (Fig. 5a) showed an appreciable intercept which indicated the presence of reverse reaction of products. The ratio of intercept to slope was 94.1 which was in good agreement with the slope-to-intercept ratio, ($K_{\mathrm{eq.}} = 77$) [16] obtained from the plot of $(\Delta A)^{-1}$ *vs* $[\mathrm{N_2H_4PhCl}]^{-1}$ (Fig. 4b).

The pH-observed rate constant profile (k_{obs}), which is quite similar to those of the [$\mathrm{Ru^{III}(HEDTA)(H_2O)}$] substitution reactions [6,18], is shown in Fig. 5b. A sharp increase in k_{obs} in the pH range 2.0–4.5 is attributed to the acid dissociation equilibrium of the carboxylic acid of the HEDTA ligand, since the dissociation of the proton of the bound $\mathrm{N_2H_4Ph^+}$ in the pH range investigated here was not observed in the pH-metric titration of 1 : 1 K[$\mathrm{Ru^{III}(HEDTA)Cl}$]·$\mathrm{2H_2O}$ and [$\mathrm{N_2H_4PhCl}$]. Thus, the pH dependence in Fig. 5b is attributed to the participation of two types of $\mathrm{Ru^{III}}$–EDTA complexes in Eq. (1) as indicated in reactions (2) and (3).

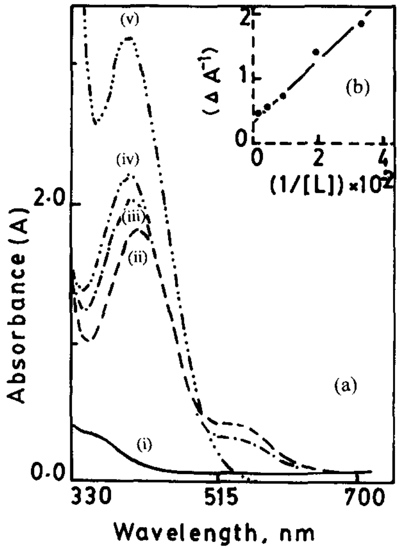


Fig. 4. (a) Absorption data of [$\mathrm{Ru^{III}(HEDTA)(H_2O)}$] (2 mM) immediately after the addition of $\mathrm{N_2H_4PhCl}$ at 25°C. $10^3 \times$ [$\mathrm{N_2H_4PhCl}$]: (i) 0.0, (ii) 0.5, (iii) 1.0, (iv) 2.0, (v) 10 M. pH 2.8. (b) Plot of the reciprocal absorbance change (ΔA^{-1}) at 420 nm *vs* the reciprocal $\mathrm{N_2H_4PhCl}$ concentration. [$\mathrm{Ru^{III}(HEDTA)(H_2O)}$] (1 mM) was dissolved in 0.2 M $\mathrm{CH_3COONa}$ and $\mathrm{H_2SO_4}$ mixture at 25°C. pH = 2.8.

$$[\mathrm{Ru^{III}(HEDTA)(H_2O)}] \overset{K_a}{\rightleftharpoons} [\mathrm{Ru^{III}(EDTA)(H_2O)}]^- + \mathrm{H^+} \quad (1)$$

$$[\mathrm{Ru^{III}(HEDTA)(H_2O)}] + \mathrm{N_2H_4Ph^+} \xrightarrow{k_1} [\mathrm{Ru^{III}(HEDTA)(N_2H_4Ph)}]^+ + \mathrm{H_2O} \quad (2)$$

$$[\mathrm{Ru^{III}(EDTA)(H_2O)}]^- + \mathrm{N_2H_4Ph^+} \xrightarrow{k_2} [\mathrm{Ru^{III}(EDTA)(N_2H_4Ph)}] + \mathrm{H_2O} \quad (3)$$

The rate expression for the above reactions can be expressed as

$$K_{\mathrm{obs}} = \{k_1[\mathrm{H^+}] + k_2K_a\}\{[\mathrm{N_2H_4Ph^+}]\}/\{[\mathrm{H^+}] + K_a\} \quad (4)$$

Where $K_a = 2.37$. From the plot of K_{obs} $\{[\mathrm{H^+}] + K_a\}/[\mathrm{N_2H_4Ph^+}]$ *vs* [$\mathrm{H^+}$], the second-order rate constants k_1 and k_2 were evaluated as 0.98 and 36.85 $\mathrm{M^{-1}\,s^{-1}}$, respectively, which were found to be larger (about two orders of magnitude) than the values of the corresponding hydrazinium complexes [12].

Mechanism of electroreduction of phenylhyrazinium complexes

Figure 6a depicts the voltammetric (sampled DC and CV) responses of $[Ru^{III}(HEDTA)(N_2H_4Ph)]Cl \cdot 2H_2O$, which showed the characteristic absorption band at 440 nm (Fig. 6b) in 0.2 M CH_3COONa and H_2SO_4 mixture at pH 2.8. Three reduction waves identical to those given in Fig. 1a were observed in sampled DC (Fig. 6a, part i). The first two waves at ($E_{1/2}$) -0.175 and -0.254 V were poorly resolved, while the third appeared as a low, intense wave at -0.417 V. The CV response in Fig. 6a part ii had further confirmed that the reduced species at -0.175, -0.254 and -0.417 V were coupled to some complex chemical reactions. In the exhaustive electrolysis at -0.5 V *vs* SCE, $[Ru^{III}(HEDTA)(N_2H_4Ph)]Cl \cdot 2H_2O$ consumed total charge equivalent to three electrons per Ru atom, which produced one equiv. ammonia and aniline. The CV of the reduced solution exhibited a pair of cathodic and anodic peaks close to those at -0.270 and -0.185 V, respectively, as shown in Fig. 4a part (ii) or those of the aquo complex. On the basis of these results, the mechanisms for the electroreduction of phenylhydrazinium adducts $[Ru^{III}(HEDTA)(N_2H_4Ph)]^+$ and $[Ru^{III}(EDTA)(N_2H_4Ph)]$ in Figs 1 and 2 are as shown in Scheme 1.

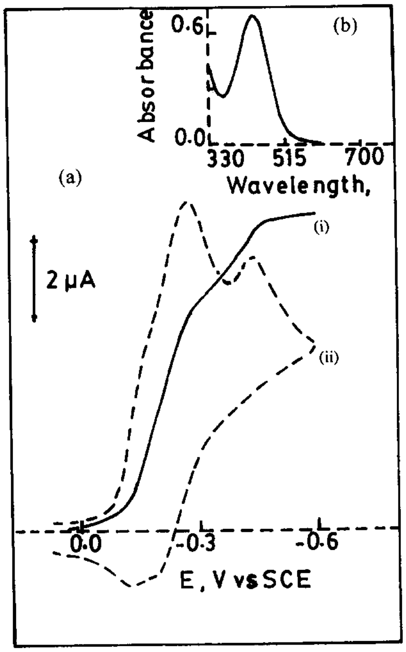


Fig. 6. Voltammetric responses: (i) sampled DC; (ii) CV at scan speed = 0.1 V s^{-1} and (b) absorption spectrum of $[Ru^{III}(HEDTA)(N_2H_4Ph)]Cl \cdot 2H_2O$ (1 mM) in 0.2 M CH_3COONa and H_2SO_4 mixture at 25°C, pH, 2.8.

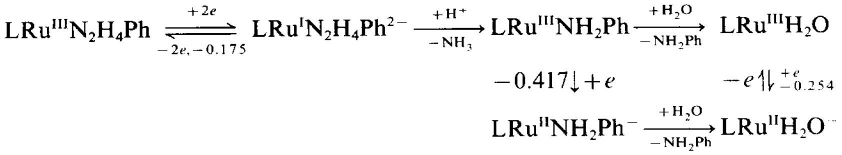
It is significant to note that the addition of $PhNH_3Cl$ to a solution of $[Ru^{III}(HEDTA)(H_2O)]$ under the present experimental conditions showed no remarkable change in the voltammetric behaviour of the $Ru^{III/II}$ couple and the absorption spectra of the latter. In other words, this accounts for the very low stability of $LRu^{III}NH_2Ph$ and $LRu^{II}NH_2Ph^-$ complexes in solution, as predicted in Scheme 1.

Catalytic reduction of phenylhydrazine

Phenylhydrazine hydrochloride (100 equiv.) in 0.2 M CH_3COONa and H_2SO_4 mixture (pH 2.8 or 1.9) containing one equiv. $K[Ru^{III}(HEDTA)Cl] \cdot 2H_2O$ was electrolysed at -0.200 V *vs* SCE in order to estimate the catalytic activity of the Ru^I–EDTA complexes of phenylhydrazine. As expected, phenylhydrazine was reduced to give NH_3 and NH_2Ph, justifying the first reduction wave at ($E_{1/2}$) -0.175 V as a multi-electron wave. The quantity of ammonia produced in the 10-h reaction was linear (Fig. 7) and consistent with the mechanism shown in Scheme 2. The turnover number, with respect to moles of ammonia formed per mole of catalyst per hour, is 5.98 at pH 2.8 and 2.82 at pH 1.9, and the coulombic efficiency was 100%.

The reduced solution, after 10 h electrolysis, showed all the electrochemical features that are shown in Figs 1 and 2 and produced ammonia when electrolysis was continued further, at the turnover rate found before. This proved that the efficiency of the metal remained intact during the turnover of phenylhydrazine reduction.

The data presented here, and previously, attests to the excellent ability to ruthenium metal, in its EDTA complexes, in transferring electrons from the external electron source (Hg electrode) to the bound N—N bonds, and the superior electron conducting nature of the Ru—N bond of nitrogenous (hydrazines/azide)



$$\begin{tikzcd}
LRu^{III}N_2H_4Ph \arrow[r, shift left, "+2e"] & LRu^{I}N_2H_4Ph^{2-} \arrow[l, shift left, "{-2e,\,-0.175}"] \arrow[r, "+H^+", "-NH_3"'] & LRu^{III}NH_2Ph \arrow[r, "+H_2O", "-NH_2Ph"'] \arrow[d, "{-0.417}"', "+e"] & LRu^{III}H_2O \arrow[d, shift left, "{+e,\,-0.254}"] \\
 & & LRu^{II}NH_2Ph^- \arrow[r, "+H_2O", "-NH_2Ph"'] & LRu^{II}H_2O^- \arrow[u, shift left, "-e"]
\end{tikzcd}$$

Where L = HEDTA or EDTA

Scheme 1.

$$\begin{aligned}
\mathrm{LRu^{III}NHPhNH_3} &\rightleftharpoons \mathrm{LRu^{I}NHPhNH_3^{2-}}\\
\mathrm{LRu^{I}NHPhNH_3^{2-}} &\rightarrow \mathrm{LRu^{III}NHPh^{2-} + NH_3}\\
\mathrm{LRu^{III}NHPh^{2-} + H^+} &\rightarrow \mathrm{LRu^{III}NH_2Ph^-}\\
\mathrm{LRu^{III}NH_2Ph^-} &\rightarrow \mathrm{LRu^{III}NHPhNH_3 + NH_2Ph}\\
\mathrm{LRu^{III}NH_2Ph^- + H_2O} &\rightarrow \mathrm{LRu^{III}H_2O^- + NH_2Ph}\\
\mathrm{LRu^{III}H_2O^- + N_2H_4Ph^+} &\rightarrow \mathrm{LRu^{III}NHPhNH_3 + H_2O}
\end{aligned}$$

Scheme 2.

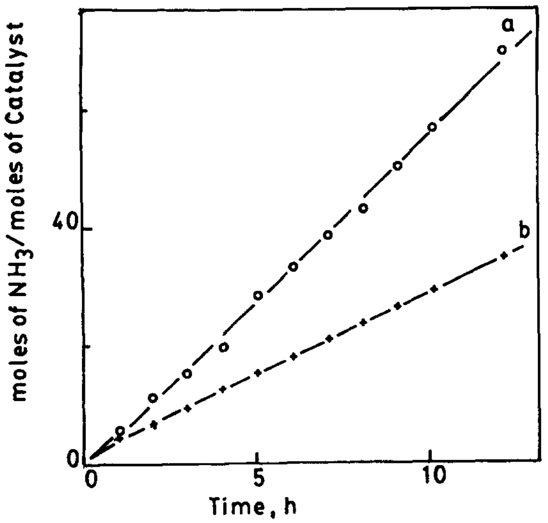


Fig. 7. Plot of moles of NH_3 per mole of $[Ru^{III}(HEDTA)(H_2O)]$ *vs* electrolysis time (h) at the initial pH (a) 2.8, (b) 1.9.

compounds. Apparently, these intrinsic properties of the metal were not altered by a change in the N—N bond order from 1.0 to 2.5, or phenyl ring substitution on the coordinated N of the $N_2H_5^+$ ion. However, the turnover rate of formation of NH_3 with N_2H_4PhCl was found to be less than the expected value (of one-half) of the turnover rate obtained with $N_2H_5HSO_4$ [12]. This slight deviation could be attributed to the combined effects of hydrophobic nature and steric and electrostatic repulsions in the reduced complexes, caused by the phenyl ring present on the bound NHPh group.

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