Electrochemical Reduction of the Dichloro(3,6-diazaoctane-1,8-diamine)-rhodium(III) Cation, *cis*-α-$[Rh(trien)Cl_2]^+$

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The electrochemical reduction of *cis*-α-$[Rh(trien)Cl_2]^+$ [trien = triethylenetetramine (3,6-diazaoctane-1,8-diamine)] has been studied using polarography and controlled potential electrolysis. The polarographic half-wave potential was found to depend on the pH above *ca.* 6.0; this was attributed to the catalysed hydrolysis of the starting complex to the corresponding chloroaqua or chlorohydroxy ion by rhodium(I), which was the initial product of the electrochemical reduction. Below pH *ca.* 6.0, no such conversion occurs because the rhodium(I) is removed rapidly from the system by reaction with H_3O^+ to form a rhodium(III) hydride.

There have been relatively few reports regarding the electrochemistry of rhodium(III). Some of these[1-3] have reported values of the polarographic half-wave potential ($E_{\frac{1}{2}}$) for a series of complexes, but no detailed study was carried out on the mechanism of the electrode reaction although it was established that the majority of the complexes underwent an irreversible two-electron reduction to, initially, a complex of rhodium(I).

A detailed electrochemical study of the complex ion *trans*-$[Rh(en)_2Cl_2]^+$ (en = ethylenediamine) in aqueous solution[4-6] using the techniques of cyclic voltammetry, controlled potential electrolysis, and chronocoulometry proved that the initial product of the electrochemical reduction was $[Rh(en)_2]^+$, but that this species underwent a series of reactions such that the final products of the electrode reaction were dependent on pH and on the potential at which the electrolysis was carried out. Thus it was possible to identify amongst the products of the electrode reaction *trans*-$[Rh(en)_2Cl(OH)]^+$, the hydride *trans*-$[Rh(en)_2H(OH)]^+$, mercury adducts, and $[Rh(en)_2]^+$, which under certain circumstances was strongly adsorbed on the mercury electrode.

A brief polarographic study[7] of the tris(dithioacetylacetonato) complex of rhodium(III) in acetone again established that the complex underwent a diffusion-controlled, irreversible, two-electron reduction. It was also suggested that the Rh^I product was strongly adsorbed on the mercury, or that possibly a mercury adduct was formed.

The only detailed polarographic studies of complexes of rhodium(III) have been conducted on *trans*-$[Rh(py)_4Cl_2]^+$[8] and $[Rh(NH_3)_5(OH)]^{2+}$.[9] Both these were shown to undergo a two-electron reduction with formation of a hydride by reaction of the initially formed Rh^I with water; in the case of the reduction of $[Rh(NH_3)_5(OH)]^{2+}$, the hydride was identified as $[Rh(NH_3)_5H]^{2+}$. The effect on the polarographic half-wave potential of varying the concentrations of H^+, Cl^-, and NH_3 was also investigated so that it was possible to identify the nature of the species actually reduced at the electrode.

The only apparent exception to the general two-electron reduction to Rh^I is with tris- and bis-(bipyridyl)[10] and -(1,10-phenanthroline)[11] complexes of rhodium(III) where it was found that more than two electrons (up to four) were transferred to the complex. This was due to some, at least, of the electrons being transferred to the extensively delocalised orbitals on the ligand rather than to the rhodium itself.

As part of a study of the factors influencing the behaviour of rhodium complexes as catalysts in homogeneous reactions, we have investigated the electrochemical properties of complexes of rhodium(III) because of their importance in the catalytic sequence.[12,13] We report here a detailed electrochemical study of the complex cation[14] *cis*-α-$[Rh(trien)Cl_2]^+$ (trien = triethylenetetramine) using the techniques of d.c. polarography and controlled potential electrolysis. No comparable study of a rhodium(III) complex with this geometry appears to have been reported.

Experimental

Buffer solutions were made from Britton–Robinson stock solution (0.04 mol dm^{-3} acetic acid, 0.04 mol dm^{-3} boric acid, and 0.04 mol dm^{-3} phosphoric acid). A measured volume (12.5 cm^3) of this solution was run into a 25 cm^3 flask, the required amount of 0.2 mol dm^{-3} sodium hydroxide solution was added, and the volume was made up with 0.2 mol dm^{-3} potassium nitrate solution, thus maintaining a constant concentration of supporting electrolyte throughout the pH range. The chloride concentration was varied in a similar manner by adding KCl.

The complex *cis*-α-$[Rh(trien)Cl_2]Cl\cdot H_2O$ was prepared as described previously;[14] its electronic spectrum was in agreement with the previous report [$\lambda_{max.}$ 352 and 288 nm (ε 240 and 210 dm^3 mol^{-1} cm^{-1})]. The complex was stable in acid and neutral solution but above pH *ca.* 10 the rate of hydrolysis became significant and so fresh stock solutions of the complex (2.5×10^{-3} mol dm^{-3}) in deionised water were prepared every 2 days. Suitable volumes of the stock solution were then diluted with a buffer solution to give the required final solution.

Classical d.c. polarography was carried out using a Radiometer Polariter PO4(d) instrument; the capillary employed had the following characteristics: $m = 3.074$ mg s^{-1}, $t = 3.3$ s when h(corr.) = 64.8 cm. For the controlled potential electrolysis experiments a vessel of about 50 cm^3 volume was filled with doubly distilled mercury to a depth of about 1 cm. Electrical contact with the mercury was made by a platinum wire electrode set in glass. The complex solution (25 cm^3 of 0.001 mol dm^{-3}) was then added, and the cell completed with a reference electrode and platinum anode both separated from the solution by sintered glass. A pH combined glass reference electrode and nitrogen inlet were also included. The mercury cathode, anode, and reference electrodes were connected to a Witton T6 Tutorial Potentiostat and the current was passed through a 2.2 ohm resistor. The voltage drop across this resistor was recorded on a Servoscribe recorder as a means of following the current changes during the electrolysis. The quantity of electricity passed was calculated from the area under the voltage–time curve.

Electronic spectra were recorded on a Pye-Unicam SP 8-100 spectrophotometer using silica cells. Changes in the electronic

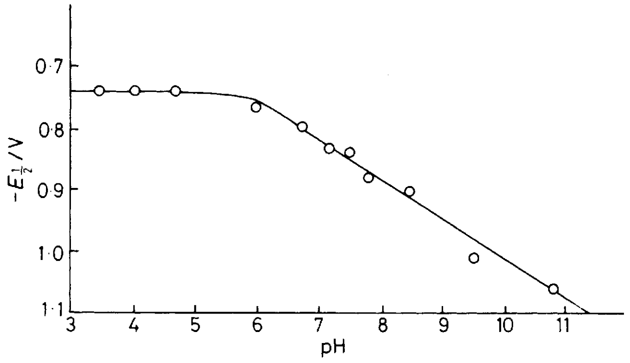

Figure. Variation of the polarographic half-wave potential ($E_{\frac{1}{2}}$) with pH for the complex ion *cis*-α-$[Rh(trien)Cl_2]^+$

Table 1. Variation of $E_{\frac{1}{2}}$ with pH for the complex ion *cis*-α-$[Rh(trien)Cl_2]^+$ (complex concentration 10^{-4} mol dm^{-3}; $E_{\frac{1}{2}}$ values relative to s.c.e.)

pH	$-E_{\frac{1}{2}}/V$ [a]	$-E_{\frac{1}{2}}/V$ [b]
3.46	0.74	
4.02	0.74	
4.70	0.74	
6.00	0.765	
6.75	0.80	0.685
7.20	0.835	0.685
7.50	0.84	0.685
7.84	0.885	0.70
8.00	0.88	0.72
8.50	0.905	0.73
9.54	1.01	0.74
10.8	1.06	0.72

[a] Main wave. [b] Pre-wave.

Table 2. Variation of $E_{\frac{1}{2}}$ with $[Cl^-]$ for the complex ion *cis*-α-$[Rh(trien)Cl_2]^+$ at fixed values of pH (complex concentration 10^{-4} mol dm^{-3}; $E_{\frac{1}{2}}$ values relative to s.c.e.)

pH	$[Cl^-]$/mol dm^{-3}	$-E_{\frac{1}{2}}/V$
3.5	10^{-4}	0.74
	0.0784	0.755
	0.296	0.745
7.2 [a]	10^{-4}	0.835
	0.016	0.95
	0.0784	0.965
	2.00	1.04
7.84 [b]	10^{-4}	0.885
	0.0784	1.015
	0.154	1.03
	0.296	1.045
10.8	10^{-4}	1.06
	0.0784	1.09
	0.296	1.11

[a] $dE_{\frac{1}{2}}/d(pCl)$ = 0.040 V per pCl unit. [b] $dE_{\frac{1}{2}}/d(pCl)$ = 0.045 V per pCl unit.

spectra during the controlled potential electrolysis experiment were followed in a separate run by using 75 cm^3 of a 0.001 mol dm^{-3} solution of the complex and pumping the solution *via* plastic tubing through a ' flow through ' silica cell in the sample compartment of the spectrophotometer.

Results and Discussion

Polarography.—The polarographic waves for 10^{-4} mol dm^{-3} solutions of the complex ion *cis*-α-$[Rh(trien)Cl_2]^+$ in buffer solutions between pH 3.46 and 10.8 fell into two distinct groups (Figure and Table 1). From pH 3.46 to about pH 5.5 the waves were single steps of nearly constant half-wave potential. At higher values of pH there was a marked pH dependence: the half-wave potentials varied linearly with pH and with a slope of −0.059 V per pH unit. At the same time a pre-wave became apparent, beginning as a small disturbance at pH *ca.* 6.45 and increasing with increasing pH until by pH 8 it accounted for about 20% of the limiting current. At higher values of pH the pre-wave remained of constant height.

At all values of pH the height of the pre-wave was directly proportional to the height of the mercury column (corrected for back pressure) and it was therefore concluded that this wave was due to adsorption of the reduction product.

For all waves the total heights (adsorption plus main wave) were directly proportional to the concentration of complex over the pH range 3.46—9.5 though the gradients of the wave-height–concentration plot decreased at higher pH. For example, at pH 7.6 the gradient was 13.8 μA l $mmol^{-1}$ while at pH 9.5 it had decreased to 6.2 μA l $mmol^{-1}$.

To establish the extent to which the reductions were diffusion-controlled the total wave-height was plotted against the square root of the corrected height of mercury. Up to about pH 7.6 these plots were linear, of gradient 0.17 μA $cm^{-\frac{1}{2}}$, and passed through the origin. At high pH however the gradients were markedly lower, though the plots were still linear, and significant intercepts on the current axis were noted. For example, at pH 9.3 the gradient was 0.04 μA $cm^{-\frac{1}{2}}$ and the intercept 0.48 μA.

From these observations it is clear that there is a change from diffusion control of the polarographic current at low pH to a mixture of diffusion and kinetic (or catalytic) control of the current as the pH increases.

In the region of diffusion control the Ilkovic equation can be used to estimate the number of electrons (n) involved in reduction of the complex ion. For this purpose a value of 4.4×10^{-6} cm^2 s^{-1} was taken for the diffusion coefficient.[2] The results ranged from 3.5 to 4.2 over the pH range 3.5—7.6. Since the simple reduction of a rhodium(III) complex to rhodium(I) should require n to have the integral value of 2, there appears to be some additional reaction. Further evidence for this view comes from the logarithmic analysis of the waves. According to the theory of irreversible waves [15] the plots of potential (E) against $\log(i/i_l - i)$ should be linear and of gradient $-0.054/\alpha n_A$ where i = current at potential E, i_l = limiting current, α = transfer coefficient, and n_A = number of electrons involved in the rate-determining step. The results obtained gave αn_A values which varied with pH (in parentheses):

0.68 (3.46), 0.76 (4.70), 1.28 (7.20), 1.52 (9.54)

Since α is most likely to have a value between 0.3 and 0.7, and this may vary with potential it is reasonable to proceed on the assumption that n_A has the value 2.

The effect of an excess of chloride ion on half-wave potential at various values of pH was investigated (Table 2 shows typical results). In solutions of pH 3.5 and pH 10.8 the excess of chloride had no effect, but between these values $E_{\frac{1}{2}}$ moved to more negative values as the chloride ion concentration was increased. The variation of $E_{\frac{1}{2}}$ with pCl was linear, the gradient being about 0.04 V per pCl unit, and the value of αn_A at constant pH remained constant as the chloride ion concentration changed.

The dependence of $E_{\frac{1}{2}}$ on pH and on pCl can only be explained [15,16] if the reduction of the electroactive species involves the participation of the hydrogen ion and chloride ion. The gradient of the $E_{\frac{1}{2}}$–pCl plot points to the reducible species having one chloride ion less than the original complex, and as the dichloro ion is known to be hydrolysed in aqueous solution,[14,17,18] the ion which is most likely to be reduced under the conditions in which chloride ion concentration affects $E_{\frac{1}{2}}$ is the chloroaqua ion formed by hydrolysis [reaction (i)]. Even if the chloroaqua ion is not the actual species reduced, this ion must be the source of the reducible species.

$$cis\text{-}\alpha\text{-}[\mathrm{Rh(trien)Cl_2}]^+ + \mathrm{H_2O} \rightleftharpoons cis\text{-}\alpha\text{-}[\mathrm{Rh(trien)Cl(H_2O)}]^{2+} + \mathrm{Cl^-} \quad \text{(i)}$$

A difficulty with this mechanism is that hydrolysis of the dichloro ion is generally slow,[14,17,18] and the establishment of equilibrium (i) demands that both forward and backward reactions be reasonably fast. This anomaly can be explained if some rhodium(I) is present, because it is well established [4,5,19] that in neutral or basic solution rhodium(I) can catalyse the substitution reaction of similar complexes of rhodium(III) by an inner-sphere redox reaction. Rhodium(I) is of course produced in the electrode reaction, and so the equilibrium can readily be set up at the surface of the mercury as soon as reduction commences. The requirement of neutral or basic conditions for the catalytic action also explains why $E_{\frac{1}{2}}$ is independent of pCl at low pH. The fact that a polarographic wave is observed in acid solution shows that the dichloro ion can be reduced directly. The half-wave potential for the reduction of the dichloro ion must be close to that for reduction of the chloroaqua ion (otherwise two waves would be observed) and equilibrium (i) must lie well to the right when it is set up (otherwise the chloroaqua ion would not be the chief electroactive species). Just as the dependence of $E_{\frac{1}{2}}$ on pCl points to the participation of the chloride ion, so the dependence on pH in solutions of pH greater than about 5.5 is indicative of an electrode reaction involving the hydrogen ion. The direction and rate of variation of $E_{\frac{1}{2}}$ (-0.059 V per pH unit) is evidence of a simple acid–base reaction in which the electroactive species acts as an acid.[15] In the present case the most probable equilibrium, in view of the well known tendencies of aqua cations to act as acids in solution,[20] is (ii).

$$cis\text{-}\alpha\text{-}[\mathrm{Rh(trien)Cl(H_2O)}]^{2+} + \mathrm{H_2O} \rightleftharpoons cis\text{-}\alpha\text{-}[\mathrm{Rh(trien)Cl(OH)}]^+ + \mathrm{H_3O^+} \quad \text{(ii)}$$

Here the acid species is the chloroaqua ion.

While the effects of chloride and hydrogen ion on the half-wave potential provide extremely strong evidence that the ion which is electroactive in neutral or basic solution is the chloroaqua ion, this ion can account for the consumption of only two electrons in its reduction to rhodium(I), and the height of the polarographic waves requires that four electrons be used per rhodium(III) complex ion. However, controlled potential electrolysis experiments provide evidence that the reduction of chloroaqua ion is accompanied by reduction of hydrogen ion, except at very high pH.

Electrolysis at Controlled Potential.—Solutions of 10^{-3} mol dm^{-3} cis-α-[Rh(trien)Cl$_2$]$^+$ were electrolysed using a mercury cathode at -1.2 V *vs.* the saturated calomel electrode (s.c.e.). (This potential corresponded to the top of the waves.) All solutions were stirred with a magnetic stirring bar on top of the mercury pool, and both pH and the electronic absorption spectrum were monitored during electrolysis. In all cases nitrogen gas was passed for 10 min before and during electrolysis.

With unbuffered 0.2 mol dm^{-3} KCl as supporting electrolyte, the pH rose very rapidly, reaching pH 8.9 after 2 min and 9.96 after 10 min. As the current approached its background value of about 0.50 mA after about 50 min, the pH levelled off near pH 11.2. During the electrolysis spectral peaks at 352 and 288 nm due to the dichloro ion were replaced by a broad shoulder at 295 nm (ε 582 dm^3 mol^{-1} cm^{-1}). The total electricity passed during complete electrolysis was 5.610 coulomb [about 16% more than necessary for the complete reduction of all rhodium(III) to rhodium(I)]. When 0.2 mol dm^{-3} KNO$_3$ was used as supporting electrolyte, the total quantity of electricity passed was 8.035 coulomb, which is some 66% more than necessary for reduction of rhodium(III) to rhodium(I). However, the final spectrum and pH were identical with those obtained when KCl was used as supporting electrolyte.

Different behaviour was observed on electrolysing using buffer solutions of pH 3.5, 8.0, and 10.0 as supporting electrolytes. In all these cases the electrolysis current did not decay to the expected background of about 0.50 mA (as with the unbuffered solutions) but fell only to between 2 and 4 mA.

During electrolysis at pH 3.5 and 8.0, the spectrum of the reactant ion was replaced by a peak at 300 nm (ε 460 dm^3 mol^{-1} cm^{-1}). At pH 10.0 the final spectrum was identical with that obtained in the unbuffered solution, *i.e.* a shoulder at 295 nm (ε 582 dm^3 mol^{-1} cm^{-1}).

When the electrolysis was conducted at pH 11.4 the current decayed to a small value and the quantity of electricity passed corresponded to $n = 1.95$. The final spectrum was again identical with that obtained in the unbuffered solution. In all these experiments no spectroscopic evidence was obtained for any intermediates, *i.e.* the spectrum of the reactant ion was replaced gradually by that of the final product as the electrolysis proceeded.

Previous work [4–6,8,9] on the electrochemistry of rhodium(III) has shown that the initial product of electrochemical reduction is a rhodium(I) species which may undergo an acid–base type reaction to form a hydride according to (iii). At higher

$$\mathrm{Rh^+} + \mathrm{H_3O^+} \rightleftharpoons [\mathrm{RhH(H_2O)}]^{2+} \quad \text{(iii)}$$

values of pH equilibrium (iii) will lie to the left, so that the concentration of Rh$^{\mathrm{I}}$ increases as the pH increases. It would thus be expected that the final product of the controlled potential electrolysis of cis-α-[Rh(trien)Cl$_2$]$^+$ at an acid pH would be a hydride of probable formula cis-α-[Rh(trien)H(H$_2$O)]$^{2+}$. The electronic spectrum of this species has been reported [21] as showing a peak at 300 nm, and this is consistent with the position of the final peak observed in controlled potential electrolysis at pH 3.5 and 8.0. Unfortunately the molar absorptivity found here (460 dm^3 mol^{-1} cm^{-1}) is much greater than that reported previously (108 dm^3 mol^{-1} cm^{-1}); this discrepancy will be discussed in the next section. If we accept that the hydride is the final product in buffer solutions, the spectral change during electrolysis is accounted for by the production of the hydride in equilibrium with a rhodium(I) species according to (iv). In unbuffered solutions in which

$$[\mathrm{Rh(trien)}]^+ + \mathrm{H_3O^+} \rightleftharpoons cis\text{-}\alpha\text{-}[\mathrm{Rh(trien)H(H_2O)}]^{2+} \quad \text{(iv)}$$

the pH becomes high, or in buffered solutions of high pH, the favoured species will be rhodium(I) rather than the hydride, and so the different spectroscopic changes observed with unbuffered solutions are explicable.

The difference in current consumption between buffered and unbuffered solution can be explained if the hydride is electroactive according to (v). The participation of such a

$$cis\text{-}\alpha\text{-}[\mathrm{Rh(trien)H(H_2O)}]^{2+} + \mathrm{e^-} \longrightarrow [\mathrm{Rh(trien)}]^+ + \tfrac{1}{2}\mathrm{H_2} + \mathrm{H_2O} \quad \text{(v)}$$

reaction can also account for the consumption of more than two electrons per complex ion in the polarographic reduction, as (iv) and (v) together are equivalent to the catalytic reduction of hydrogen ion. A similar sequence has been observed previously in the case of *trans*-[Rh(en)$_2$H(H$_2$O)]$^{2+}$, which is effective in catalysing the reduction of hydrogen ion to dihydrogen gas at a mercury cathode in the pH range 3—11.

The extent to which these two reactions participate will depend on pH through the control exerted by (iv). Under conditions of high pH the catalytic reduction is inhibited because equilibrium (iv) lies well to the left, so that at pH 11.4 virtually no catalytic reduction of hydrogen ion occurs and the quantity of electricity consumed corresponds exactly to reduction of the rhodium(III) reactant to rhodium(I). At more acid pH, the catalytic cycle is operative so that in buffered solutions below *ca.* pH 10.00 the limiting electrolysis current is high. The increase of pH during the electrolysis of the unbuffered solution arises from the consumption of hydrogen ion by reaction (iv) followed by (v). The eventual cessation of the electrolysis is due to the shift of equilibrium (iv) to the left as the pH increases.

General Discussion.—The polarographic results require that the nature of the rhodium(III) species which is reduced at the mercury electrode depends on the pH of the solution. Below about pH 6.0 the reducible species is the dichloro ion as shown in (vi). At higher pH the chloroaqua ion becomes reducible

$$\textit{cis}\text{-}\alpha\text{-}[\mathrm{Rh(trien)Cl_2}]^+ + 2e^- \longrightarrow [\mathrm{Rh(trien)}]^+ + 2\mathrm{Cl}^- \quad \text{(vi)}$$

$$\textit{cis}\text{-}\alpha\text{-}[\mathrm{Rh(trien)Cl(H_2O)}]^{2+} + 2e^- \longrightarrow [\mathrm{Rh(trien)}]^+ + \mathrm{Cl}^- + \mathrm{H_2O} \quad \text{(vii)}$$

[reaction (vii)]. The change from (vi) to (vii) as the chief electrode reaction occurs because the chloroaqua ion becomes more abundant than the dichloro ion in the region near the electrode, and this is caused by the aquation equilibrium (i) being set up under the influence of the catalyst rhodium(I) which is produced at the electrode.

The current consumed in the controlled potential electrolysis experiments and the heights of the polarographic waves demand that other reactions participate in the overall reduction process. The involvement of the hydride *cis*-α-[Rh(trien)H(H$_2$O)]$^{2+}$, for the presence of which there is strong evidence, in reactions (iv) and (v) not only explains the amount of electricity used but can also account for the change in reducible species which occurs near pH 6.0. Under acid conditions rhodium(I) is converted into the hydride [through reaction (iv)] and so the concentration of rhodium(I) is reduced to a level which prevents it functioning as a catalyst for the aquation of the dichloro ion.

If the reduction mechanism proposed is correct then controlled potential reduction should result in the dichloro–chloroaqua equilibrium being established in the bulk solution as well as in the diffusion layer at the electrode surface because of the production of large amounts of rhodium(I) to act as catalyst. No spectroscopic evidence of a change from dichloro to chloroaqua ion was obtained, but it is likely that the changes would not be observable because of the close similarity of the two spectra [dichloro,[14] $\lambda_{\text{max.}}$ 352 and 288 nm (ε 240 and 210 dm^3 mol^{-1} cm^{-1}); chloroaqua,[17] $\lambda_{\text{max.}}$ 347 and 295 nm (ε 212 and 157 dm^3 mol^{-1} cm^{-1})] and by the spectrum of the reduction product being much more intense than that of the reactants below 330 nm. Spectral changes due to conversion of dichloro into chloroaqua ion would therefore be disguised by formation of product whether the product is chiefly rhodium(I) at high pH or the rhodium(I)–rhodium(III) hydride mixture at pH less than about 10.0. The similarity of the spectra of the products of electrolysis at pH 3.5 and 8.0 is surprising, as it might have been expected than an acid–base equilibrium involving the species *cis*-α-[Rh(trien)H(H$_2$O)]$^{2+}$ and *cis*-α-[Rh(trien)H(OH)]$^+$ would be set up, and be accompanied by a change in the electronic spectrum as the pH was altered. However, it was noted previously[5] during the electrolysis of *trans*-[Rh(en)$_2$H(H$_2$O)]$^{2+}$ that no change occurred in the electronic spectrum of this rhodium complex as the pH increased from 3 to 11.

It was observed earlier that the absorbance due to the hydride is different from that previously reported[21] for the complex prepared by reaction between sodium tetrahydroborate and *cis*-α-[Rh(trien)Cl$_2$]$^+$ and characterised as the hydride by its n.m.r. spectrum. It is possible that this preparation did not result in quantitative conversion of starting material, which would result in a low value for ε. The higher value (460 dm^3 mol^{-1} cm^{-1} at 300 nm) is consistent with known trends[22] in the spectra of species of type [RhN$_4$XY], where N$_4$ represents four nitrogen ligands [*e.g.* (NH$_3$)$_4$, (en)$_2$, trien] and X and Y are the same or different. For example,[4,5] *trans*-[Rh(en)$_2$H(H$_2$O)]$^{2+}$ has $\lambda_{\text{max.}}$ 295 and 257 nm (ε 323 and 272 dm^3 mol^{-1} cm^{-1}) and on passing from *trans* to *cis* geometry the value of ε for the lowest energy *d–d* transition usually increases. It would therefore be expected that ε at 300 nm would be greater than 323 dm^3 mol^{-1} cm^{-1} for the complex *cis*-α-[Rh(trien)H(H$_2$O)]$^{2+}$.

Reaction (iv) can also explain how the polarographic adsorption current changes with pH. If [Rh(trien)]$^+$ were adsorbed on mercury, this would give rise to an adsorption pre-wave. But in acid solution reaction (iv) could effectively remove the adsorbed material to form the rhodium(III) aqua hydride and so the pre-wave should be more apparent in solutions of high pH, as is indeed the case. The occurrence of adsorption of such species has previously been reported in the case of [Rh$^{\mathrm{I}}$(en)$_2$]$^+$,[5] and in the electrochemical reduction of tris(dithioacetylacetonato)rhodium(III)[7] and *trans*-dichlorotetrapyridinerhodium(III).[8] The catalytic currents observed in the controlled potential experiments using buffered solutions are largely unaffected by adsorption effects since stirring the mercury interface will continually produce a fresh mercury surface.

One observation that we are unable to account for fully is that at high pH the polarographic current becomes limited by the rate of a slow, *i.e.* kinetically controlled, reaction. Reaction (ii), at high pH, will lie well to the right, and the kinetic control of the polarographic current probably arises through the decrease in the rate of the reverse of this reaction because of the diminished hydrogen ion concentration. The kinetic control does not arise through any change in the rate of formation of the chloroaqua or chlorohydroxy species by the rhodium(I)-catalysed inner-sphere redox reaction. In fact, it would be expected that the rate of this catalysed reaction would increase as the pH increases because of the greater concentration of rhodium(I) present through reaction (iv).

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