758. *Polarographic Reduction of Complexes of Rhodium*(III)

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Polarographic studies on a number of halogenoammino-complexes of rhodium(III) have shown that the primary reduction process is a two-electron step.

IT has been shown previously[1] that certain reducing agents catalyse the syntheses of complexes of rhodium(III) with nitrogenous ligands. We have suggested that hydridic intermediates may occur in such systems, although, in related work,[2] lower valency states of rhodium were thought to be responsible for the catalysis. Molecular hydrogen may also be activated by complexes of rhodium(III), and, in such cases,[3,4] it seems likely that an intermediate hydride is formed, as in the case of certain iridium complexes, where the hydrides have been isolated.[5]

The polarographic method is capable, in principle, of distinguishing between the primary processes

$$Rh^{3+} + e^- \longrightarrow Rh^{2+} \ (n = 1)$$
$$Rh^{3+} + 2e^- \longrightarrow Rh^{+} \ (n = 2)$$

We therefore examined several halogenoamminorhodium(III) complexes by means of polarography.

Rhodium(III) complexes have previously been studied on several occasions polarographically. However, in the light of our present knowledge of the chemistry of rhodium, it is quite clear that in most cases the solutions used contained *mixtures* of several complexes, despite the usual assumption that a single species only was present. For example, even refluxed solutions of rhodium trichloride and pyridine contain[6] only the isomers of trichlorotripyridinerhodium(III), and not the hexakispyridinerhodium(III) cation, as was assumed.[7a] Values of n in much previous work have therefore rested on diffusion coefficients which are greatly in error, since the assumption as to the nature of the electro-active species have usually been incorrect. Polarographic data on well-characterised complexes of rhodium(III) are collected in Table 1.

Chlororhodium(III) species in particular have given rise to variable conclusions. Cozzi and Pantani[8] found fairly large variation of $E_{\frac{1}{2}}$ with the concentration of the supporting electrolyte, hydrochloric acid, suggesting that more species were present in solution than they considered. Recently, Magee and Douglas,[9] using larger chloride-ion concentrations,

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[1] R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J.*, 1965, 1951.

[2] J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 658.

[3] R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 1964, 284.

[4] J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Comm.*, 1965, 17.

[5] L. Vaska, Proc. 8th Internat. Congr. Co-ordination Chem., 1964, p. 99.

[6] R. D. Gillard and G. Wilkinson, *J.*, 1964, 1224.

[7] (*a*) J. B. Willis, *J. Amer. Chem. Soc.*, 1944, **66**, 1067; (*b*) S. A. Repin, *J. Appl. Chem. U.S.S.R.*, 1947, **20**, 46, 55; (*c*) G. Semerano and E. Gagliardo, *Ricerca Sci.*, 1950, **20**, 1676.

[8] D. Cozzi and F. Pantani, *J. Inorg. Nuclear Chem.*, 1958, **8**, 385.

[9] R. J. Magee and W. H. Douglas, *J. Inorg. Nuclear Chem.*, 1964, **10**, 1707.

TABLE 1

Polarographic results for complexes of rhodium(III)

Complex	Supporting electrolyte	$E_{\frac{1}{2}}$ *	n	Ref.
$[Rh(SCN)_6]^{3-}$	KSCN (0·9M)	−0·39	2	*a*
$[Rh(NH_3)_5Cl]^{2+}$	$NaNO_3$ (1M)	−0·96	2	*a*
	K_2SO_4 (0·5M)	−0·96	2	*a*
	NH_4Cl (1M)	−0·93	2	*a*
	NH_3 (1M) NH_4Cl (1M)	−0·93	2	*a*
$[Rh(CN)_6]^{3-}$	KCN (1M)	−1·54	2	*b*
" $RhCl_3$ "	$HClO_4$ (0·5M)	−0·39	2	*c*
$[Rh(C_2O_4)_2Cl_2]^{3-}$		−0·43	2	*c*
$[Rh(C_2O_4)_3]^{3-}$	$H_2C_2O_4$ (0·5M)	−0·83	2	*c*

[a] J. B. Willis, *J. Amer. Chem. Soc.*, 1944, **66**, 1067. [b] W. P. Griffith and G. Wilkinson, *J.*, 1959, 2757. [c] A. Wagnerova, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2076.

* v relative to S.C.E.

studied solutions which still contained a large fraction of mixed chloro-aquo-species. The presence of such species is obvious from the comparison of the quoted electronic spectra [9] with those of well-characterised complexes.[10] Because of the probable presence of polymeric complexes in solutions of rhodium(III) in chloride media, manifested by the strong electronic absorption bands observed [3] in the near-ultraviolet region, we re-investigated the reduction of hexachlororhodate(III) ion using sodium hexachlororhodate(III) dissolved in sodium chloride solution; the complex does not aquate detectably during the experiment. $E_{\frac{1}{2}}$ was −0·19v (relative to the S.C.E.) with $n = 2$. It is relevant that, in reductions of ferric ion with molecular hydrogen, catalysed by solutions containing $[RhCl_6]^{3-}$, it has been suggested,[11] on kinetic grounds, that the intermediate responsible is $[HRhCl_5]^{3-}$; such an ion could certainly form from the further reaction of the first reduction product of the polarographic process.

The validity of results obtained by using the coulombic method [8] is questionable, since for the chloropentamminerhodium(III) cation the coulombic method gave $n = 3$, while an accurate polarographic determination [12] on this cation showed it to undergo a two-electron reduction. We have shown that hydridopentamminerhodium(III) ion is slowly oxidised by water. This would account for the high value obtained in the coulombic study; the coulombic results for the hexachlororhodate(III) system are questionable also, in view of the likelihood of hydridic species intervening in the equilibria.

Analytical methods for determining rhodium by means of polarography have repeatedly recommended [7] use of a pyridine medium. The assumption [7a,9] has been, incorrectly, that dissolving rhodium trichloride in aqueous pyridine gave the hexakispyridinerhodium(III) cation. In this work, using *trans*-dichlorotetrapyridinerhodium(III) chloride, $E_{\frac{1}{2}}$(I) was found to be −0·39 with $n = 2$, under varying conditions. It is noteworthy that on treatment with hydride ion, this complex cation yields [13] a hydrido-species, as in

$$trans\text{-}[Rhpy_4Cl_2]^+ + H^- \longrightarrow trans\text{-}[Rhpy_4ClH]^+ + Cl^-$$

A two-electron reduction can be regarded [14] as equivalent to the formation of either Rh^I or Rh^{III}–H. A second polarographic wave is observed for this salt with $E_{\frac{1}{2}}$(II) = −0·95; however, this is probably not a simple electron step between two stable species. Although n is approximately 1, i_d(II) does not bear a constant relation to i_d(I). This second step is due to the further reduction, possibly of the ligand, of a reduced species formed in step I, *e.g.*, $[Rhpy_4HCl]^+$, particularly since the high $E_{\frac{1}{2}}$ observed is characteristic [15] of hydridic species.

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[10] (*a*) C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 500; (*b*) W. Wolsey, C. Reynolds, and J. Kleinberg, *Inorg. Chem.*, 1963, **2**, 463.

[11] J. F. Harrod and J. Halpern, *Canad. J. Chem.*, 1959, **37**, 1933.

[12] A. A. Vlček, *Disc. Faraday Soc.*, 1958, **26**, 164.

[13] J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J.*, 1964, 3168.

[14] A. A. Vlček, *Prog. Inorg. Chem.*, 1963, **5**, 371.

[15] A. A. Vlček, *Prog. Inorg. Chem.*, 1963, **5**, 372.

Similar results were obtained for the cation *trans*-$[Rhpy_4Br_2]^+$; data are collected in Table 2. The polarographic behaviour of the *trans*-dichlorobisbipyridylrhodium(III) cation is not as simple as that of its pyridine analogue; a polarographic wave is observed, but accurate measurements were not obtained because the pronounced maxima, due probably to the unsaturated ligand, could not be suppressed.

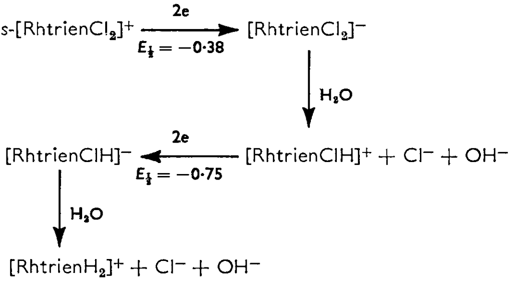
TABLE 2

Polarographic results for *trans*-$[Rh(amine)_4XY]$

Complex	Concn. (mm./l.)	$E_{\frac{1}{2}}$(I) *	i_d (μA)	$D^{\frac{1}{2}}$	$m^{\frac{2}{3}}t^{\frac{1}{6}}$	n	$\lambda_{max.}$	$E_{\frac{1}{2}}$(II) *
$Rhen_2Cl_2^+$	1	−0·79	6·7	$2·3 \times 10^{-3}$	2·2	2	406	—
	0·2	−0·79	1·4	$2·3 \times 10^{-3}$	2·2	2		
$Rhen_2I_2^+$	0·47	−0·70	2·8	$2·1 \times 10^{-3}$	2·2	2	462	—
$Rhen_2BrCl^+$ ...	1	−0·77	5·8	$2·2 \times 10^{-3}$	2·3	2	417	—
$Rhpy_4Cl_2^+$	0·62	−0·39	3·5	$2·1 \times 10^{-3}$	2·2	2	411	−0·95
$Rhpy_4Br_2^+$	1	−0·28	3·0	$2·1 \times 10^{-3}$	2·2	2	425	−0·92

* v relative to S.C.E.

For complexes of the type *trans*-$[Rhen_2XY]^+$, where X and Y are halides, similar results were obtained for the first reduction step. Again, n is 2, in line with our observations [13] on the chemical reductions of such complexes. For these *trans*-cations, no second wave derived from further reduction of the monohydride could be found. For the *cis*-isomers of these cations, $[Rhen_2X_2]^+$, where X = halide, only ill-defined polarographic waves could be obtained and no accurate measurements were possible. However, with *cis*-dichlorotriethylenetetraminerhodium(III) chloride, two waves were observed, with $E_{\frac{1}{2}} = -0·38$ and $-0·75$, both having n approximately 2. We have previously demonstrated the existence [13] of both the mono- and di-hydridic species, $[RhtrienClH]^+$ and $[RhtrienH_2]^+$, and it seems likely that the two waves observed may be accounted for by the scheme:



The only other case where two polarographic waves were observed was for the dichloro(ethylenediaminediacetatodiacetic acid)rhodate(III) anion,$[Rh(H_2EDTA)Cl_2]^-$. This was previously studied by Russian workers,[16] who claimed that $E_{\frac{1}{2}} = -0·75$ with $n = 3$. We find that this is a two-step reduction, with $E_{\frac{1}{2}}(I) = -0·73$, and $E_{\frac{1}{2}}(II) = -0·97$. The two steps are approximately equal, $i_d(I) \simeq i_d(II)$. Using a value for the diffusion coefficient derived from the conductivity of potassium ethylenediaminetetra-acetatocobaltate(III), whereby $D^{\frac{1}{2}} = 2·5 \times 10^{-3}$, we find $n = 4$, so that $n_I = n_{II} = 2$. The diffusion coefficient derived from the rhodium complex itself is not useful, because of the presence of ionisable protons in the complex, the pK value being about 4. The electronic spectra of the dichloro-complex and of its dibromo-analogue show shifts of the longest wavelength band to shorter wavelengths when the complexes are treated with borohydride ion. Isosbestic points are observed for the reactions. We previously found [13] that in the

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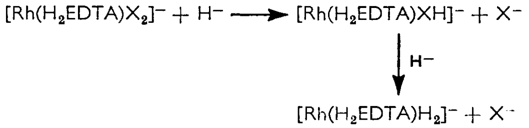
[16] N. A. Ezerskaya and V. N. Filimonova, *Russ. J. Inorg. Chem.*, 1963, **8**, 424.

TABLE 3

Spectra data for reactions $[Rh(H_2EDTA)X_2]^- + H^- \longrightarrow [Rh(H_2EDTA)XH]^- + X^-$

	$[Rh(H_2EDTA)X_2]^-$		Isosbestic point		$[Rh(H_2EDTA)XH]^-$	
X	$\lambda_{max.}$	ε		X	$\lambda_{max.}$	ε
Cl	402	400	377	Cl	370	360
Br	418	460	392	Br	375	500

spectrochemical series $H^- > Cl^- > Br^-$, and the data collected in Table 3 for these systems agree with the formation of hydridic species, as in



$$\begin{tikzcd}[Rh(H_2EDTA)X_2]^- + H^- \arrow[r] & {[Rh(H_2EDTA)XH]^- + X^-} \arrow[d, "H^-"] \\ & {[Rh(H_2EDTA)H_2]^- + X^-}\end{tikzcd}$$

However, we have not been able to establish the presence of rhodium–hydrogen bonds by means of proton magnetic resonance.

Vlček [12,14] has pointed out that the process $M^{n+} \longrightarrow M^{m+}$ (where $n > m$) involves addition of electrons to the lowest unoccupied orbitals of the metal, and that the half-wave potential should be related to the lowest energy *d–d* electronic transitions for similar complexes. An attempt was made recently [9] to interpret polarographic results for complexes of rhodium(III) in this way. However, examination of the quoted [9] electronic spectra shows that the assumption that the solutions used contained complexes of the type $[RhX_6]^{n+}$, where X = Cl^-, SCN^-, py, NH_3, or CN^-, is unjustified. If spectrophotometric and polarographic results are to be meaningfully correlated, it is essential that clearly defined complexes must be used.

When, in our complexes of the type *trans*-$[Rhen_2XY]^+$, $E_{\frac{1}{2}}$ is plotted against $\Delta\nu$ [12] (the difference between the observed frequencies of ${}^1T_{1g} \longleftarrow {}^1A_{1g}$ in $[Rh(NH_3)_6]^{3+}$ and ${}^1E_g \longleftarrow {}^1A_{1g}$ of the complex), a straight line is obtained with slope $-3{\cdot}3 \times 10^{-5}$v cm.$^{-2}$. The relationship between ease of reduction and the energy of the lowest unoccupied orbital is similarly clear in the case of *trans*-$[Rhpy_4X_2]^+$, where X = Cl or Br. Unfortunately, the di-iodo-complex is thermodynamically unstable, readily losing pyridine.

The present results show that, in these ammine complexes, rhodium(II) is not formed. It seems probable that this valency state cannot be responsible for the catalysis by reducing agents of reactions of rhodium(III) complexes. The remaining question of whether the catalytic species is Rh^I or Rh^{III}–H is not settled, though the activation of molecular hydrogen by rhodium(III) complexes favours the hydridic concept, which is also supported by the existence of hydridic species in many complexes of rhodium(III) containing non-π-bonding ligands.

EXPERIMENTAL

Preparative details for the complexes used are given in our earlier work.

Polarograms were obtained by using a Tinsley Mark 19 recording instrument with a dropping mercury electrode. Some details are given in Table 2. Reductions were irreversible. The supporting electrolyte was potassium chloride (0·1M), though a number of confirmatory experiments were performed with potassium chloride (0·01M) as supporting electrolyte. In nearly every case, a solution of gelatine (0·01%) was added to suppress the marked maximum common to nearly all complexes of the platinum metals.

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