43. Electrochemical Investigation of Potassium Heptacyanorhenate(III) in Aqueous Solution

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The electrochemistry of potassium heptacyanorhenate(III) in aqueous solution was studied by cyclic and by rotating disk voltammetry at planar microelectrodes. The results are consistent with a single, reversible electron transfer: $Re(CN)_7^{3-} + e \rightleftarrows Re(CN)_7^{4-}$ with $E_0' = 643$ mV *vs. NHE*. A single protonation equilibrium is observed: $Re(CN)_7^{4-} + H^+ \rightleftarrows Re(CN)_7H^{3-}$ with p$K = 1.31$ determined from combined voltammetric and pH data. The Re–CN bond appears to be kinetically inert, and none of the cyano complexes in other oxidation states of Re claimed in the literature was found in the potential range -2 V to $+1$ V.

Introduction. – Cyano complexes of rhenium in the oxidation states 0 to VI have been claimed since more than thirty years [1] [2], and the literature is summarized in a review by *Griffith* [3]. In a more recent paper by *Griffith et al.* [4], the existence of many of these species has been questioned, and only two of them, *viz.* $Re(CN)_7^{4-}$ [5] and $Re(CN)_6^{5-}$ [6] [7], were confirmed. The claims concerning the pentacyano complex of Re^{II} [8], the hexacyano complexes of Re^0 [9], Re^{II} [8] [10], Re^{III} [11] [12], and Re^V [11] [14], and the octacyano complex of Re^V [11] [14] have been re-interpreted in terms of different stoichiometries and charges, or of mixtures of other species. Only $Re(CN)_8^{2-}$ [11] was neither confirmed nor re-interpreted [4]. A single-crystal X-ray structure of $K_4Re(CN)_7 \cdot 2H_2O$ [15] has since then confirmed the supposed stoichiometry [5] and has shown a pentagonal bipyramidal geometry of the $Re(CN)_7^{4-}$ ion.

The electrochemistry of the cyanorhenates has not been studied since their critical re-examination [4]. In an early report, the oxidation of $Re(CN)_6^{5-}$ and of $[Re^{II}(CN)_4 \cdot Re^{IV}(CN)_4]^{2-}$ has been investigated by potentiometric titration with $Fe(CN)_6^{3-}$ [1] [2]. By the same technique, $E_0' = +0.72$ V has been found for a couple assigned as $Re(CN)_6^{3-/4-}$ [16]. The reduction of supposed $Re(CN)_8^{3-}$ has been studied polarographically, and the reduction products were believed to contain Re^{-1} in 2M KCl and Re^I in 0.1M KCN, respectively [17].

In view of these conflicting reports, a re-investigation of the electrochemistry of the cyanorhenates appeared to be called for. In this work, we have studied the possibilities of reduction and oxidation of the most extensively characterized species, $Re(CN)_7^{4-}$ [4] [15] in aqueous solution.

Results and Discussion. – The starting material for our electrochemical study, $K_4Re(CN)_7 \cdot H_2O$, was prepared according to *Griffith et al.* [4]. The stoichiometry of the compound was established both by elemental analysis and by potentiometric deter-

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mination of its molecular weight. Its spectral characteristics are the same as for the respective dihydrate [4] (see *Experimental*).

Cyclic voltammograms of 1 mM aqueous solutions of $Re(CN)_7^{4-}$ in the presence of various supporting electrolytes ($NaClO_4$, KCl, and HCl (1M); H_2SO_4 (0.5M)) were recorded using different electrode materials (Hg, Pt, and glassy carbon). Within the accessible potential range (+ 1 V to − 2 V [18]), a single wave in the anodic region but none in the cathodic region was observed. Attempts to extend the potential range by using solvents such as CH_3CN, DMF, or DMSO were unsuccessful due to the poor solubility of the Re compound. Addition of 18-crown-6 (frequently used to solubilize potassium salts in aprotic solvents [19]) did not sufficiently increase the solubility of our compound, and, therefore, the electrochemistry of $Re(CN)_7^{4-}$ could only be studied in aqueous solution.

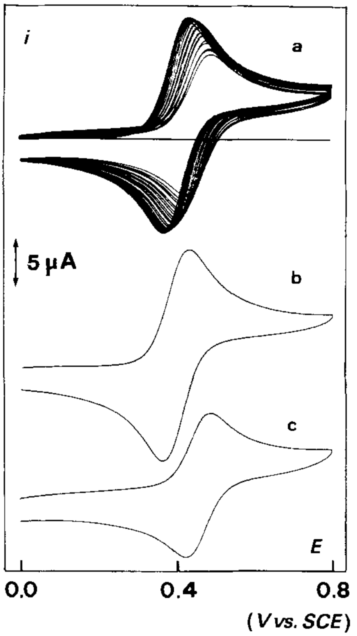

Fig. 1. *Cyclic voltammograms of $K_4Re(CN)_7 \cdot H_2O$ in aqueous 1 M KCl at 25°* (15 ml of 0.86 mM soln. titrated with totally 10 ml of 1M HCl (*a*); prior to the addition of HCl (*b*); after addition of 10 ml of 1M HCl, pH 0.34 (*c*))

The cyclic voltammograms of $Re(CN)_7^{4-}$ show but a single wave (*Fig. 1*), the characteristics of which for scan rates between 10 and 500 mVs^{-1} can be summarized as follows: i) The ratio of anodic to cathodic peak currents, i_{pa}/i_{pc}, is 1.03 and does not depend on the scan rate (theoretically, 1.00 is expected for perfect reversibility [18]). ii) A plot of the peak current *vs.* square root of scan rate is perfectly linear, as it is predicted by the *Randles-Sevcik* equation [18] [20] for a reversible system. iii) The position of the anodic and cathodic peaks, E_{pa} and E_{pc}, respectively, does not depend on the scan rate. The experimental values of $|E_p - E_{p/2}|$ and of $|E_{pa} - E_{pc}|$ are 60 ± 2 mV, *i.e.*, very close to the theoretical values of 56.5 mV and 59.0 mV, respectively, for a one-electron transfer at 25° [18] [20].

Thus, the characteristics of the observed wave are that of a reversible (*Nernstian*) one-electron transfer. The formal reduction potential E'_0 for a reversible couple is given by ½ $(E_{pa} - E_{pc})$ [20] and on this basis we find

$$E'_0(\mathrm{Re(CN)_7^{3-}/Re(CN)_7^{4-}}) = 643 \pm 3 \text{ mV } vs.\ NHE$$

$$(25°, \text{pH } 7, 1\text{M KCl or NaClO}_4).$$

Due to the linear dependence of the peak current i_p on the square root of the scan rate v, the *Randles-Sevcik* equation [18] [20]

$$i_p = 2.69 \cdot 10^5 n^{3/2} A D^{1/2} v^{1/2} C$$

(where n is the number of electrons transferred, A the surface of the electrode, and C the bulk concentration of the electroactive species) could be used to determine the diffusion coefficient D of $\mathrm{Re(CN)_7^{4-}}$. Using $n = 1$ we obtain

$$D = 5.6 \pm 0.4 \cdot 10^{-6} \mathrm{cm^2 s^{-1}}$$

(mean value from experiments with different electrodes and supporting electrolytes at 25°). This value can be compared with $D = 6.3 \cdot 10^{-6} \mathrm{cm^2 s^{-1}}$ for $\mathrm{Fe(CN)_6^{4-}}$ [21]. From the *Einstein-Stokes* equation [22], the diffusion coefficient in first approximation is inversely proportional to the cubic root of the molecular weight. A value of $D = 5.2 \cdot 10^{-6} \mathrm{cm^2 s^{-1}}$, thus, estimated for $\mathrm{Re(CN)_7^{4-}}$ is in reasonable agreement with the experimental value. This confirms the choice of $n = 1$, *i.e.* a single electron is transferred in our system.

The results obtained from cyclic voltammetry (transient method) were further confirmed using rotating disk voltammetry (stationary method). The same curves were obtained from anodic and cathodic scans, which again indicate a reversible process. The formal potential obtained by this method is

$$E'_0 = 642 \pm 2 \text{ mV } vs.\ NHE\ (25°, \text{pH } 7, 1\text{M KCl}).$$

Using the *Levich* equation [18], a value of $6.2 \cdot 10^{-6} \mathrm{cm^2 s^{-1}}$ for the diffusion coefficient was estimated.

From the results obtained by the two different methods, it can be concluded that $\mathrm{Re(CN)_7^{4-}}$, indeed, undergoes a reversible one-electron oxidation. The redox potential of the $\mathrm{Re(CN)_7^{3-/4-}}$ couple does not depend on the supporting electrolyte (KCl, $\mathrm{NaClO_4}$) and, moreover, is unaffected by the presence of KCN. Thus, both the oxidized and the reduced form of the complex appear to be kinetically inert. However, addition of acid shifts the wave towards more positive potentials as can be seen from *Fig. 1*. The cyclic voltammogram at low pH shows the same characteristics as the one at pH 7 (*vide supra*). There is no indication of an irreversible reaction occurring in acidic solution since the original voltammogram is observed after re-adjusting the pH to ≥ 5 by adding base.

The shift of E'_0 towards more positive values in acidic solution is well documented for other cyano complexes, *e.g.* $\mathrm{Fe(CN)_6^{4-}}$, and is due to N-protonation of coordinated cyanide [23].

The variation of the formal potential as a function of pH in our system is displayed in *Fig. 2*. Such a dependence can be explained by assuming a reversible protonation of the reduced species [18]

$$\mathrm{Re(CN)_7^{4-} + H^+ \rightleftarrows Re(CN)_7H^{3-}}$$

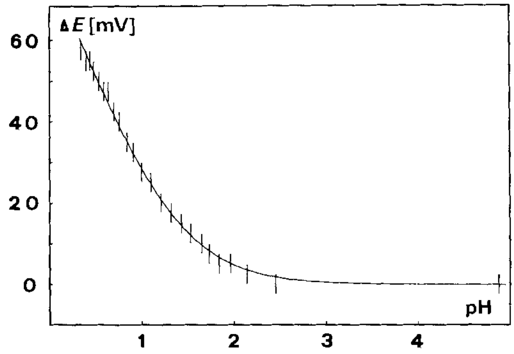

Fig. 2. *Shifts of the formal potential of the Re(CN)$_7^{4-/3-}$ couple as a function of pH.* Experimental data: bars of length 4σ. Calculated curve: ——— (Conditions are as in *Fig. 1*).

which leads to

$$\Delta E\,[\mathrm{mV}] = -59\ln(1 + K\cdot[\mathrm{H^+}]).$$

A non-linear minimisation program [24] was used in order to find the value of the dissociation constant K which yields the closest description of the observed potential shifts by corresponding calculated ones. The best fit with an overall standard deviation $\sigma = 1.2$ mV (see *Fig. 2*) was obtained for

$$\mathrm{p}K = 1.31 \pm 0.02\ (25°,\ 1\,\mathrm{M}\ \mathrm{KCl}).$$

Attempts to determine an additional protonation constant did only yield insignificant improvements of the fit. Thus, under the experimental conditions used only a single chemical process occurs, namely the reversible protonation of $\mathrm{Re(CN)_7^{4-}}$.

Compared to $\mathrm{Fe(CN)_6^{4-}}$ (pK = 3.25 (I = 0.2M) [25], E_0' = 0.48 V (1M KCl) [26]), $\mathrm{Re(CN)_7^{4-}}$ is both more difficult to oxidize and to protonate. The rough correlation between pK and E_0' indicates that oxidation and protonation occur in a similar fashion. Since protonation of cyano complexes is known to take place at the N-atoms [23], it seems likely that the electron which is removed from $\mathrm{Re(CN)_7^{4-}}$ originates from an orbital with a high electron density on the cyano N-atoms.

In contrast to $\mathrm{Fe(CN)_6^{3-}}$, which is kinetically labile with respect to dissociation of cyanide, no indication of such a behaviour has been found in our system.

An interesting observation is that the formal potential of $\mathrm{Re(CN)_7^{3-/4-}}$ in acid solution (E_0' = 706 ± 3 mV, pH 0.3, 0.5M $\mathrm{H_2SO_4}$) agrees well with that of the alleged $\mathrm{Re(CN)_6^{3-/4-}}$ couple (E_0' = 0.72 V, 0.5M $\mathrm{H_2SO_4}$ [16]). It has been suspected [4] that the stoichiometry and valence state suggested in [16] were in error, and that in fact heptacyanorhenate(III) was studied. Indeed, *Griffith et al.* [4] were able to isolate $\mathrm{K_4Re(CN)_7 \cdot 2\,H_2O}$ using (among others) the method given in [16]. The present study nicely corroborates the conclusion that the supposed $\mathrm{K_4Re^{II}(CN)_6}$ is in fact $\mathrm{K_4Re^{III}(CN)_7}$.

To conclude, the results of this study are surprisingly simple. In aqueous solution, only two processes are observed, namely the one-electron oxidation and the protonation of $\mathrm{Re(CN)_7^{4-}}$. None of the other redox pairs claimed in the literature is found. The observed couple is reversible, and both reduced and oxidized forms appear to be kinetically robust. Electrochemical oxidation, thus, promises to be an efficient way of preparing the still uncharacterized heptacyanorhenate(IV).

Experimental. – *Materials.* Potassium perrhenate (*Fluka, puriss.*) was used as received. Other chemicals for preparative work were of *purum* or *puriss.* grade. Anal.-grade reagents were used throughout in the quant. anal. procedures and in the electrochemical measurements. Deionized and distilled H_2O was used. K_2ReCl_6 was prepared by H_3PO_2 reduction of $KReO_4$ in concentrated HCl [27] [28]. Anal. calc. for K_2ReCl_6: K 16.39, Re 39.03; found: K 16.39, Re 39.05.

Tetrapotassium Heptacyanorhenate Monohydrate. The synthesis was achieved according to *Griffith et al.* [4] [5] by reacting K_2ReCl_6 (1 g) with KSeCN (20 g) [31] and KCN (2 g) under N_2. The extraction of the mixture was made with deoxygenated CH_3OH in a *Soxhlet* apparatus under N_2 for 12 h. The residue containing the insoluble cyano complex was suspended in boiling CH_3OH (7 ml), and enough deoxygenated H_2O was added (*ca.* 2–3 ml) to dissolve the complex. A greenish-black residue was filtered off, and, after cooling in an ice bath, 0.52 g $K_4Re(CN)_7 \cdot H_2O$ of 99% purity (UV/VIS) was obtained. Further addition of CH_3OH (10 ml) afforded another 0.09 g of the product of 91% purity. Anal. calc. for $K_4Re(CN)_7 \cdot H_2O$ (542.7): C 15.5, H 0.4, N 18.0, K 28.8, Re 34.3; found: C 15.2, H 0.5, N 17.8, K 28.7, Re 34.0 (from cerimetric titration, a molecular weight of 544.7 was determined). UV/VIS (H_2O, 25°; λ [nm]/$\varepsilon \cdot 10^{-3}$ [$\mathrm{lmol^{-1}cm^{-1}}$]): 203/24.5 (sh); 214/31.0 (max.); 236/12.4 (min.); 252/20.2 (max.); 270/5.4 (sh) ([4]: 203/25.0; 214/30.0; 253/20.0; 272/5.7).

Quantitative Analysis. Potassium was determined gravimetrically as the tetraphenyl borate [29]. Rhenium was oxidized to ReO_4^- with alkaline H_2O_2, precipitated as the tetraphenylarsonium salt, and weighed [30]. C, H, and N was determined in the Mikrolabor, ETH Zürich.

Cyclic Voltammetry. The set-up consisted of a potentiostat (*Metrohm E506*), a signal generator (*Metrohm E612*), and a *x-y* recorder (*Hewlett-Packard 7040A*). A standard three-electrode arrangement was used with a counter electrode (Pt coil) and a reference electrode (Ag/AgCl/KCl 3M, $E(25°) = 208$ mV *vs. NHE*, or $Hg/HgCl_2/$KCl sat. (= *SCE*), $E(25°) = 244$ mV *vs. NHE* [18] [21]). Working electrode was either a hanging Hg drop (= HMDE) or a planar microelectrode (Pt or glassy carbon disks of 1–3-mm diameter mounted in *Teflon*). The solid electrodes were pretreated prior to each measurement according to [21] [26] [32]. Cyclic voltammograms were recorded for 1 mM aq. solns. of $K_4Re(CN)_7$ in the presence of 1M supporting electrolyte in a titration vessel thermostatted at 25 ± 0.1° under N_2.

Rotating Disk Voltammetry. An instrument (*Metrohm 628-10*) was used which allowed to rotate a glassy carbon microelectrode of 3-mm diameter at 1500 rpm. Voltammograms were recorded with 10, 50, and 100 $\mathrm{mVs^{-1}}$, the other experimental conditions were as described above.

Combined Potentiometric and Voltammetric Titration. To 15.0 ml of a 0.86 mM soln. of $K_4Re(CN)_7 \cdot H_2O$ in 1M KCl, 10 ml of 1M HCl were added stepwise by an automatic burette (*Metrohm Dosimat*). The pH was measured after each addition of acid using a combined glass electrode (*Metrohm*) and a pH meter (*Metrohm 632*). From the same soln., the cyclic voltammogram was recorded using a glassy carbon electrode (scan rate 0.1 $\mathrm{Vs^{-1}}$).

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