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Reduction of Aqueous Rhenate(VII) at a Platinum Electrode

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The electrochemical reduction of aqueous ReO_4^- at a platinum electrode has been studied by cyclic voltammetry. The reduction product has been identified as ReO_2.

It has been established that the reduction of rhenate (VII) occurs via a chemical step involving adsorbed hydrogen atoms produced in the electrode reaction.

The oxidation of ReO_2 in aqueous solutions was found to be a spontaneous reaction with a rate depending on pH and on its previous history.

An interpretation of the reactivity of ReO_2 and ReO_4^-, with respect to TcO_2 and TcO_4^-, is also given.

Introduction

The reduction of aqueous rhenate(VII) on platinum and mercury electrodes has been studied by several authors[1–16].

The reported results present however a confusing picture because evident disagreement both on the nature of the electrochemical reaction and also on the valence changes comes out. In fact the number of electrons involved in the electrochemical reduction ranges from eight to one depending on the author consulted.

The present paper deals with the electrochemical reduction of rhenate(VII) in $HClO_4$, HCl and NaOH solutions, at stationary platinum electrodes; the main technique employed in this investigation was the cyclic voltammetry.

This work represents a further contribution to the knowledge of the voltammetric behaviour of Group VII B compounds[17].

Experimental

Chemicals and Reagents

The solutions of $KReO_4$ (Alfa Inorganics) were prepared by dissolving wheighed amounts of this product in the different media. These media were aqueous $HClO_4$ (4*M* and 1*M*), aqueous HCl (4*M*, 1*M* and 0.1*M*) and aqueous NaOH (1*M* and 0.1*M*). Ammonium exachlororhenate [$(NH_4)_2ReCl_6$, Schuchardt] was employed without further purification to record reference spectra and to prepare rhenium dioxide. ReO_2 was obtained by adding NaOH to an aqueous solution of $(NH_4)_2ReCl_6$[18]; the growing of the precipitate particles was gained by addition of a small amount of H_2SO_4.

Tetrabutylammoniumperrhenate was prepared by dissolving a wheighed amount of rhenium metal (Alfa Inorganics) with hydrogen peroxide solution and successively neutralizing the formed perrhenic acid with tetrabutylammonium hydroxide (Fluka). The white precipitate was crystallized from ethanol and dried in a vacuum oven at 50° C.

Acetonitrile (R. P. Erba) was purified by distilling repeatedly from phosphorus pentoxide and stored on molecular sieves (3 Å).

The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was prepared from perchloric acid and tetrabutylammonium hydroxide, recrystallized from ethanol and finally dried in a vacuum oven.

99.99% nitrogen was employed to remove oxygen from the test solution.

Apparatus

The experiments were carried out in H shaped cells with cathodic and anodic compartments separated by sintered glass disks at the temperature of 20° C.

All the potential values are referred to an aqueous satured calomel electrode (SCE); this reference electrode was connected to the cell by appropriate salt bridges. The electrical apparatus employed in the cyclic voltammetric experiments and in controlled potential electrolyses have been already described[17].

The experimental concentrations of rhenate(VII) ranged from $5 \times 10^{-4}M$ to $10^{-2}M$.

Results

Cyclic voltammetric tests performed on $KReO_4$ in $HClO_4$ solutions did not show any cathodic peak which could be attributed to the direct rhenate(VII) reduction. In fact in the cathodic branch only a small enhancement of the poorly defined peak, corresponding to the reduction of hydrogen ions to adsorbed hydrogen[19], could be noted. In the anodic branch two different pictures could be observed (see Figure 1):

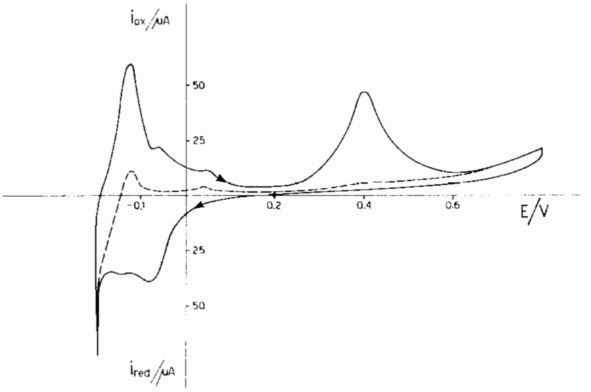

Figure 1. Cyclic voltammetric curve with stationary platinum electrode for a $5\times10^{-3}M$ $KReO_4$, $4M$ $HClO_4$ solution; scan rate $0.2\,V\,s^{-1}$.

when the potential scan was reversed as soon as the solvent discharge had been reached, no well developed anodic peak was observed (dashed line). On the contrary, if the platinum electrode was allowed to stand few seconds at the potential of hydrogen evolution, a well developed anodic peak appeared at about +0.4 V (full line in Figure 1); its height was found to be dependent on the time spent in the hydrogen discharge.

Large scale electrolyses carried out at potential values corresponding to the incoming reduction of the solvent showed that, together with hydrogen evolution, a solid deposit was formed on the platinum surface.

This layer could be observed only after some time from the start of the electrolysis and its colour changed from an initial yellow–brown to a final black. The thickness of the deposit resulted always small, even for long times of electrolysis, owing to its poor adherence on the electrode surface.

When the potential of the electrolytically covered electrode was shifted towards more positive potentials, the deposit quickly dissolved as soon as a potential of about zero volts was reached; simultaneously a large anodic current flowed.

Also the grey–black precipitate suspended in the solution dissolved, but more slowly. In addition it was noted that the deposit on the electrode after washing and drying, dissolved very slowly in the original solution even if the electrode was polarized at positive potentials (+ 1 V).

In order to gain some information about the nature of the deposit, the covered platinum foil washed, dried and wheighed, was dipped in $1M$ sulphuric acid; a known volume of cerium(IV) standard solution was added and then the excess of cerium was back-titrated with standard Fe^{2+} solution. Direct titrations were unreliable owing to the slowness of the reaction.

By assuming for the deposit the formula $ReO_2\cdot2H_2O$, the results of many redox titrations indicated that the number of equivalents of cerium spent for mol of $ReO_2\cdot2H_2O$ was slightly inferior to three.

Karl–Fischer titration data were consistent with the hypothesis that two moles of water are bound to each mol of rhenium dioxide.

In this connection we report that the same results were obtained also in the titrations with cerium(IV) of $ReO_2\cdot2H_2O$ prepared from $(NH_4)_2ReCl_6$ by the chemical procedure reported in the experimental section.

An interesting feature of both titrations was that the number of equivalents of Ce^{IV} consumed, progressively lowered with the increment of the time interval between the introduction of rhenium dioxide in the titration vessel and the addition of cerium(IV) solution.

A second test carried out to check the nature of the deposit, was to record spectra in the U. V. and visible regions of the solutions obtained by dissolving the deposit in $8M$ HCl.

These spectra strictly agreed with that exhibited by analogous solutions prepared from rhenium dioxide chemically obtained.

The results obtained in the cyclic voltammetric tests and in large scale electrolyses performed in NaOH solution were rather different from those obtained in $HClO_4$ media: no anodic peak was detectable in the reverse scan and, in addition, the layer of deposit appeared only after a long time from the beginning of the electrolysis. When the electrolysis was stopped, the solid layer dissolved more rapidly than in $HClO_4$ solutions.

However the analytical tests previously used gave again evidence that the deposit was, also in this case, rhenium dioxide.

Cyclic voltammetric tests performed on ReO_4^- in HCl solutions at an acid concentration lesser than $0.1M$, revealed again the presence of an anodic peak associated to the solvent discharge.

When the HCl concentration was increased, this anodic peak disappeared. In this last case large scale electrolyses showed that no deposit was formed at the electrode surface, while the solution became progressively yellow–green.

The spectrum of these solutions indicated the presence of the $ReCl_6^{2-}$ species[18].

In order to clarify the role of the hydrogen discharge in the rhenate(VII) reduction, hydrogen gas was bubbled into ReO_4^- acid solution in presence of platinized platinum.

The platinum surface was progressively covered by a black compound which dissolved in $8M$ HCl giving a solution whose spectrum was the same exhibited by the $ReCl_6^{2-}$ species.

To verify whether the rhenate(VII) reduction occurred only *via* a chemical reaction or also *via* a cathodic reaction simultaneous to the hydrogen discharge, electrochemical investigations were performed in acetonitrile medium.

In these experiments $(n\text{-}Bu)_4NReO_4$ was employed owing to the insolubility of $KReO_4$; cyclic voltammetric tests performed in CH_3CN, 0.1*M* TBAP solutions revealed no reduction peak attributable to the rhenate(VII) ion.

When cyclic voltammograms were recorded on solutions in which anhydrous $HClO_4$ was previously electrochemically generated[20], only the peaks associated to the H^+/H_2 system could be detected, at potential values near to zero volts[20].

On the contrary, controlled potential electrolyses carried out at potential values corresponding to the reduction of hydrogen ions gave evidence for the formation of a brown–black film on the platinum surface, also in this medium. This reduction product dissolved very quickly as soon as the electrode potential was increased to values at which the hydrogen ions reduction no longer occurred.

The ability of rhenium dioxide to dissolve in aqueous media has been tested at various pH values. When rhenium dioxide, chemically prepared, was suspended in aqueous solution, it dissolved completely with a rate increasing from acid to the basic medium. This dissolution required in any case some hours. On the contrary, rhenium dioxide freshly electrochemically generated at the electrode surface dissolved in few seconds, while the same deposit after washing and drying dissolved in several minutes.

In every case the resulting solutions were colorless and redox tests with cerium(IV) and UV spectra demonstrated that the rhenium was in the ReO_4^- state.

Finally it can be remembered that these tests, when performed in pure water, gave evidence that in the dissolution process hydrogen ions were released.

Discussion

All the experimental results give evidence that the reduction of rhenate(VII) at a platinum electrode occurs *via* a chemical reaction involving hydrogen generated in a primary electrochemical step.

In fact neither a cathodic peak nor a rhenium dioxide deposit can be observed unless the potential of the hydrogen discharge is reached.

Furthermore, the simultaneous occurrence of hydrogen evolution and electrodic rhenate(VII) reduction must be disregarded, owing to the results obtained in the voltammetric experiments carried out in acetonitrile medium.

These tests proved that rhenate(VII) ions are not directly reduced on platinum electrode even at −2.2 V (cathodic limit of the solvent); only in the presence of hydrogen ions a deposit was formed when the electrode was polarized at the potential of the cathodic reduction of the protons.

Finally, the reduction of rhenate(VII) in aqueous solutions by molecular hydrogen in presence of platinized platinum furtherly supports the following overall scheme for the reduction of rhenate(VII) at platinum electrodes:

$$3\,H^+ + 3\,e^- \rightarrow 3\,H(Pt) \qquad (1)$$

$$ReO_4^- + 3\,H(Pt) + H^+ \rightarrow ReO_2 + 2\,H_2O \qquad (2)$$

In the above mechanism ReO_4^- ions are reduced in a slow chemical step following the electrode reaction (1). H(Pt) formed in this electrode reaction is suggested to be the reducing agent, instead of molecular hydrogen, to acconunt for the indispensable presence of platinized platinum in the chemical reduction of rhenium(VII). According to this view the cathodic peak at about −0.08 V (Figure 1) is due to the hydrogen ions reduction to adsorbed hydrogen, whose small increment can be attributed to an increase of the electrode area as a consequence of the ReO_2 formation. A similar reaction pathway has been proposed also for the electrochemical reduction of technetate (VII) ions[17]. Our titration data, relative to the reduction product, indicate a valence change slightly inferior to the theoretical value of three, which corresponds to the oxidation of Re^{IV} to Re^{VII}.

In our opinion these results can be explained suggesting the occurrence, to some extent, of an oxidation of rhenium dioxide by the solvent.

This view agrees with the behaviour exhibited in aqueous solution by the chemically prepared rhenium dioxide.

The observed dissolution of rhenium dioxide with the checked formation of rhenate(VII), indicate that the systematic negative errors in the titrations with Ce^{IV} can be attributed to the occurrence of the reaction:

$$2\,ReO_2 + 4\,H_2O \rightarrow 2\,ReO_4^- + 3\,H_2 + 2\,H^+ \qquad (3)$$

It can be observed that this reaction is just the reverse of scheme (2). Oxygen is disregarded as oxidizing agent because the dissolution of rhenium dioxide occurred also in rigorously deaerated solutions.

The recovery of hydrogen ions in the dissolution tests carried out in twice distilled water confirms the above reported reaction scheme.

Furthermore, reaction (3) accounts for the change in dissolution rate by changing the pH of the aqueous solutions.

The different oxidation rate between chemically and electrochemically prepared rhenium dioxide can be explained taking into account a different growing of the precipitate in the two cases. This behaviour could be also explained by different allotropic states; in this connection we remember that the various allotropic forms of MnO_2 exhibit different reactivities[21]. On the other hand it is known that the solubility of rhenium dioxide depends on its previous history[18].

We think that the anodic current, observed as soon as the potential of the working electrode is rosen to about zero volts, is due to the oxidation of hydrogen previously generated together with rhenium dioxide.

Consequently the simultaneous disappearance of the deposit, at the same potential value, can be attributed to the occurrence of the reaction (3) which is operative as hydrogen is no longer present.

At present no experimental data surely indicate what is the process responsible of the anodic peak (Figure 1). However, by arguing form analogy with the results obtained in a previous study on technetate (VII)[17], we think that this anodic peak has to be attributed to the electrochemical oxidation to ReO_4^- of rhenium dioxide still present at the electrode surface. Hence this anodic oxidation must be considered to be competitive with the chemical reaction (3).

This hypotesis disagrees wit the report of Shropshire[11] who found an anodic process at the same potential value observed by us (+0.4 V) but attributed it to the diffusion controlled oxidation of Re^{VI} to Re^{VII}.

However his experimental results could be explained following our view, taking into account that the working electrode employed in his chronopotentiometric tests was a platinized platinum one, dipped in a solution containing both rhenate(VII) and hydrogen, which had to be produced at the basket platinum platinized electrode at his working potential value[19]. In these experimental conditions, ReO_2 is chemically produced at the platinum surface, as above reported in the "Results" section, and consequently the observed anodic process could be attributed again to the electrochemical oxidation of ReO_2.

The absence of this anodic peak in experiments carried out in NaOH solution can be explained by considering the high rate of chemical oxidation reaction (3) in alkaline medium. This reaction subtracts all the oxide formed in the cathodic branch before the potential of its electrochemical oxidation is reached.

Also in HCl solutions the absence of the anodic peak is to be attributed to the subtraction of ReO_2 from the electrode surface but, in this case, as a consequence of the formation of Re^{IV} chloride complexes. In fact, when the HCl concentration was below $0.1\,M$, the anodic peak was again detectable owing to its inability to give rhenium chloride complexes.

By comparing the reduction on platinum electrodes of rhenate(VII) and technetate(VII)[17], it appears that similar mechanisms and products are involved; however it can be observed that technetate(VII) is more easily reduced and its reduction product, TcO_2, is more stable than rhenium dioxide.

This different behaviour does not allow to suggest experimental conditions for quantitative determinations of rhenium(IV) at variance with the technetium case[17,22]. However it can be remarked that the electrochemical reduction of ReO_4^- on platinum electrodes in HCl media is a suitable method to prepare Re^{IV} chloride complexes.

The higher reducing power exhibited by ReO_2 in comparison with TcO_2 and also MnO_2 is to be connected to the well known increasing stability of the highest oxidation states of heavier elements in a transition metal group.

In this connection it can be remarked that MnO_4^- is a strong oxidizing agent, TcO_4^- is reduced by strong reductants[22] while ReO_4^- is not quantitatively reduced even by $SnCl_2$ solutions.

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