The Rest Potentials of Platinum, Rhodium and Iridium Electrodes

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The Rest Potentials of Platinum, Rhodium and Iridium Electrodes

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The reduced and oxidized platinum, rhodium and iridium electrodes were alternately dipped, as, cathode into the solutions of 1 N H₂SO₄, 1 N HNO₃, 1 N H₂SO₄ + 1/8 M K₂Cr₂O₇, 1 N HNO₃ + 1/8 M K₂Cr₂O₇, 1/4 M Cr₂O₇⁻, 1 N H₂SO₄ + 10⁻² M Ce (IV) SO₄, 1 N NaOH, 1 N NaOH + 1/8 M K₂Cr₂O₇. The potentials with respect to time were measured against a calomel electrode, (rest potentials). The electrodes were pretreated in two separate ways.

The electrode, as anode, was dipped into a 1 N solution of H₂SO₄. A current of 200 mA was passed for a period of five minutes. Then the oxidized electrode was again dipped into a same type solution with continuous flow of nitrogen while being connected to a calomel electrode in short circuit (reduced electrode).

The electrodes prepared according to the above procedure were again oxidized, anodically, for fifteen minutes under a current of 200 mA (oxidized electrodes).

Using the same electrolyte, the rest potentials for platinum, rhodium and iridium were found to have different values. The rest potentials for these metals in the solutions mentioned above were very close to the equilibrium potentials of the same metals in the oxidized state this indicates. That they were being oxidized in these solutions. The time required for such metals to reach equilibrium was shortest for iridium next for rhodium and platinum.

INTRODUCTION

The fact that the reduction of bichromate on platinum, gold and palladium electrodes occurs on the same reduction potentials of their oxides, was previously indicated by one of us [1]. Both the previous study and the present work verifies that the electrodes are oxidized and coated with a film of oxide when they are inserted in bichromate solutions.
In this study, rest potentials in various oxidizing systems have been determined to investigate whether noble metals such as platinum, rhodium and iridium are oxidized in oxidizing media.

**EXPERIMENTAL**

In this series experiment great care was taken to see that all chemicals were chemically pure and solutions were prepared with conductance water and the glass ware was made of pyrex glass. The cell used to determine the rest potentials was a three armed one. The first arm was the anode; the second arm was the cathode compartment. The reference calomel electrode was dipped within the third arm. The stopcock between the second and the third arm was kept close in order to prevent the diffusion of chloride ions.

Variations of cathode potentials with time, in various oxidizing solutions were measured against a saturated calomel electrode and apparatus used to determine the potential was Knickmessverstärker (Berlin).

The solution in the cell was kept at the same level and mixed continuously with a magnetic stirrer during experiment. The electrodes used as cathodes were platinum, rhodium and iridium wires in 3 cm length and 0.5 mm diameter.

As many investigators [1-6] have indicated current - potential and potential - time curves change in accordance with the pretreatment of the electrodes. Therefore to get reproducible curves electrodes were subjected to the same procedure [2-1], before experiment.

Reducing the electrodes: The electrode was dipped into 1 N H₂SO₄ solution as anode and a current of 200 mA was passed for five minutes. Then the oxidized electrode was dipped in a cell which contain 1 N H₂SO₄ solution through which nitrogen gas was passed continuously and the electrode was connected to a calomel electrode in short circuit. The potential of electrode, reduced against calomel was measured with a potentiometer at intervals and the reduction procedure ended 400 - 350 mV for platinum and 280 mV for rhodium and iridium. These values are given as
potentials for this metals when oxide layer produced with anodic polarization had just been removed but hydrogen adsorption had not yet began [6]. In this text the electrodes prepared in the above manner are called "reduced electrodes".

Oxidizing the electrodes: The reduced electrodes prepared with the above procedure were again oxidized, anodically, for fifteen minutes under a current of 200 mA. These electrodes are called "oxidized electrodes".

The rest potentials curves have been obtained both with oxidized and reduced electrodes.

CONCLUSIONS

As may be observed in figure 1, 2, 3 and 4 the curves of oxidized and reduced electrodes reached the same potentials value in a certain period. In figure 1 the rest potentials curves of platinum, rhodium and iridium electrodes in 1 N H₂SO₄ are shown. An oxidized platinum electrode when dipped in 1 N H₂SO₄, a potential around 1280 mV is observed, however, this potential drops until 920 mV and remained fixed thereafter. Moreover a reduced platinum electrode showed a potential of 900 mV when dipped in the same solution at the beginning. Then it rises steadily to 940 mV which is the maximum point and remained fixed around 900 mV.

The curve obtained with oxidized rhodium electrode has shown an inflection point at 1060 mV and dropped to a constant value of 770 mV. The curve obtained with reduced rhodium electrode showed a maximum of 880 mV and potential decreased slowly to 770 mV and was stable at this value. The curve of oxidized and reduced iridium electrodes reached to the same constant value (810 mV). The curve of reduced iridium electrode reaches to the maximum point at 855 mV.

Hoare [7-9] measured the potential of platinum, rhodium and iridium electrodes after oxidizing them anodically in 2 N H₂SO₄ saturated with oxygen and then measured their potentials in the same solutions. The results of this study found to be in good agreement with those of Hoare's. Bianchi and Mussini [3] found 960 mV for
Fig. 1. The rest potentials of platinum, rhodium and iridium in 1 N H₂SO₄ solution. Open figures for reduced electrodes, filled figures for oxidized electrodes. □ ▲ rhodium, ◆ ○ iridium, ◆ ◆ platinum
Fig. 2. The rest potentials of platinum electrode in various oxidizing media. Open figures for reduced electrode, filled figures for oxidized electrode: 

- +1NH₄SO₄ + 10⁻³ M Ce(IV)SO₄, X 1/8 M K₃Cr₂O₇ + 1 N HNO₃, □ 1/8 M K₃Cr₂O₇ + 1 N H₂SO₄, ▼ ▽ 1/4 MCrO₃,
- ▲ 1 N HNO₃, ■ △ 1 NH₄SO₄, ○ 1 N NaOH, [ ] 1 N NaOH + 1/8 M K₃Cr₂O₇
the rest potential of platinum electrode in 0.5 N \( \text{H}_2\text{SO}_4 \). In figures 1, 2, 3 and 4 the potential - time curves for oxidized and reduced platinum, rhodium and iridium electrodes in various solutions are shown. The equilibrium values obtained from these curves are presented in table I. In table II the theoretical values calculated by Latimer and the experimental values measured by Hoare are given.

**DISCUSSION**

As it is seen in figure 1, 2, 3, 4 and table I these three metals have different rest potentials in the same solutions. The rest potentials in acidic media are different from the normal potentials of \( \text{O}_2/\text{H}_2\text{O} \) system but these potentials are almost equal to normal potentials of electrode metal oxides given by Latimer and Hoare.

The fact that various curves in figures get fixed at certain potentials levels are equal to various metal oxides can well be understood when these potentials levels are compared with the table II. That is, there is an agreement between the maximum, noticed in the curve obtained in 1 N \( \text{H}_2\text{SO}_4 \) with the reduced rhodium electrode and the normal potential of reaction 3 determined by Hoare at table II. Similarly, there is an agreement between the maximum around 855 mV seen at the curve of reduced iridium electrode in 1 N \( \text{H}_2\text{SO}_4 \) and the normal potential of reaction 5 determined by Hoare. The rest potential found for platinum electrode in 1 N \( \text{HNO}_3 \) and the normal potential of the reaction 4 of the Latimer indicated at table II are almost the same. Oxidized rhodium electrode curve which is obtained in 1 N \( \text{H}_2\text{SO}_4 \) has an inflection point at 1060 mV. The rest potential of rhodium electrode in 1 N \( \text{HNO}_3 \) is almost the same with the above value, (1050 mV). Moreover rest potentials obtained in 1 N \( \text{NaOH} \) have shown that electrodes can be oxidized in basic media as well as in acidic media. The values of 170 mV and 140 mV for platinum and iridium respectively are close to the potentials of reactions 1 (for platinum) 2 or 3 (for iridium) in table II. For this metals the time required to reach equilibrium decreases the order of “thermodynamic nobility” in accordance with. For rhodium and iridium (Fig. 3, 4) the rest potentials obtained between 1600 and 800 mV in various
oxidizing media are cumulated in definite potential regions, but
the curves of platinum (fig 2) are dispersed between above values.
This can be explained by the fact that definite oxides are formed
on the surface of rhodium and iridium electrodes in accordance
with the oxidizing power of the solution. But in the case of plat-
inum, mixed oxides are formed on the electrode surface. Anson
and Lingane[10] had shown that the oxide film formed on the sur-
face of platinum by anodic polarization or by different oxidizing
agents were mixtures of PtO₂ and real PtO₂.

The rest potentials obtained with these electrodes in bichro-
mate solutions are different from each other as in the case of Ce
(IV) SO₄ + 1 N H₂SO₄ and have different values according to the
kind of acid present in the medium. According to Müller[11] and
Knorr[12] the surface of the electrode is coated with a film of chromic
chromate as soon as it is inserted into a chromic acid solution.
If this assumption is right, the rest potentials in chromic acid solu-
tion should be the same for both of the three electrodes. If the sur-
face of these metals are not oxidized by bichromate or chromic
acid, the phenomena would be the same (the formation of chromic
chromate) and therefore the rest potentials would be the same.

**TABLE I**

The rest potentials of platinum, rhodium and iridium electrodes
in various oxidizing media

<table>
<thead>
<tr>
<th>Medium</th>
<th>Platinum (mV)</th>
<th>Rhodium (mV)</th>
<th>Iridium (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N H₂SO₄ + 10⁻² M Ce(IV) SO₄</td>
<td>1575</td>
<td>1555</td>
<td>1525</td>
</tr>
<tr>
<td>1/8 M K₂Cr₂O₇ + 1 N HNO₃</td>
<td>1255</td>
<td>1275</td>
<td>1290</td>
</tr>
<tr>
<td>1/8 M K₂Cr₂O₇ + 1 N H₂SO₄</td>
<td>1240</td>
<td>1250</td>
<td>1275</td>
</tr>
<tr>
<td>1/4 M CrO₃</td>
<td>1160</td>
<td>1200</td>
<td>1240</td>
</tr>
<tr>
<td>1 N HNO₃</td>
<td>1075</td>
<td>1050</td>
<td>1070</td>
</tr>
<tr>
<td>1 N H₂SO₄</td>
<td>900</td>
<td>770</td>
<td>800</td>
</tr>
<tr>
<td>1 N NaOH</td>
<td>170</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>1 N NaOH + 1/8 M K₂Cr₂O₇</td>
<td>160</td>
<td>110</td>
<td>120</td>
</tr>
</tbody>
</table>
Fig. 3. The rate potentials of iodide electrode in various oxidizing media. Open figures for reduced electrode, filled figures for oxidized electrode.

- 1 N HSO₄
- 1 N H₂SO₄
- 1 N HNO₃
- 1 N NaOH
- 1 N H₂SO₄+1/8 M K₂Cr₂O₇
- 1 N HSO₄+1/8 M K₂Cr₂O₇
- 1 N H₂SO₄+1/8 M K₂Cr₂O₇

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Fig. 4. The rest potentials of iridium electrodes in various oxidizing media. Open figures for reduced electrode, filled figures for oxidized electrode.
<table>
<thead>
<tr>
<th>Electrode (metal)</th>
<th>Latimer's calculated values</th>
<th>Hoare's experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactions</td>
<td>E°(V)</td>
</tr>
<tr>
<td>Platinum</td>
<td>2OH⁻ + Pt = Pt(OH)₂ + 2e</td>
<td>-0.150</td>
</tr>
<tr>
<td></td>
<td>Pt + 2H₂O = Pt(OH)₂ + 2H⁺ + 2e</td>
<td>-0.980</td>
</tr>
<tr>
<td></td>
<td>Pt(OH)₄⁺ = Pt(OH)₆⁻ + 2e</td>
<td>-0.1 to -0.4</td>
</tr>
<tr>
<td></td>
<td>Pt(OH)₂ = PtO₂⁺ + 2H⁺ + 2e</td>
<td>-1.100</td>
</tr>
<tr>
<td>Rhodium</td>
<td>2Rh⁺ + 3H₂O = Rh₂O₃ + 6H⁺ + 6e</td>
<td>-0.870</td>
</tr>
<tr>
<td></td>
<td>2Rh⁺ + H₂O = Rh₂O + 2H⁺ + 2e</td>
<td>-0.950</td>
</tr>
<tr>
<td></td>
<td>4OH⁻ + Rh₂O₃ = Rh₂O⁺ + 2e + 2H₂O</td>
<td>&gt;-0.90</td>
</tr>
<tr>
<td></td>
<td>2OH⁻ + Rh₂O₃ = 2RhO₂⁺ + H₂O + 2e</td>
<td>&gt;-0.90</td>
</tr>
<tr>
<td>Iridium</td>
<td>Ir + 2H₂O = IrO₂ + 4H⁺ + 4e</td>
<td>-0.930</td>
</tr>
<tr>
<td></td>
<td>Ir + 4OH⁻ = IrO₂⁺ + 2H₂O + 4e</td>
<td>-0.100</td>
</tr>
<tr>
<td></td>
<td>Ir + 6OH⁻ = IrO₂⁺ + 3H₂O + 6e</td>
<td>-0.100</td>
</tr>
<tr>
<td></td>
<td>IrO₂ + 4OH⁻ = IrO₂⁺ + 2H₂O + 2e</td>
<td>-0.400</td>
</tr>
</tbody>
</table>
REFERENCES

[8.] " " " 111, 232 (1964)
[9.] " " " 110, 987 (1964)

ÖZET

Oksitli ve redükslenmiş platin, rodyum ve iridyum elektrotlar 1 N H₂SO₄, 1 N HNO₃, 1 N H₂SO₄ + 1/8 M K₂Cr₂O₇, 1 N HNO₃ + 1/8 M K₂Cr₂O₇, 1/4 M CrO₃, 1 N H₂SO₄ + 10⁻⁹ M Ce (IV) SO₄, 1 N NaOH, 1 N NaOH + 1/8 M K₂Cr₂O₇, çözeltileri içinde daldırılan, potansiyelleri doygun kalomel elektroda karşı izlenmiştir, (süknet potansiyeli).

Elektrotlar iki türlü ön muameleye tabi tutulmuştur.
1. 1 N H₂SO₄ içinde 5 dakika 200 mA de oksitlenen elektrotlar, içinde azot gazı geçirlen 1 N H₂SO₄ içinde daldırılan kalomel elektroda karşı kısa devre yapılmıştır, (redükslenmiş elektrot).
2. Yukarıdaki yolla redükslenmiş elektrotlar tekrar 15 dakika 200 mA de oksitlenmiştir, (okşitli elektrot).

Aynı çözelti içinde platin, rodyum ve iridyum elektrotların süknet potansiyellerinin birbirinden farklı olduğunu tespit edilmiştir. Yukarıdaki muhtelif çözelti içinde her üç elektrotla elde edilen süknet potansiyellerinin literatürde bu metallerin oksitleri için verilen denge potansiyellerine yakın olması, muhtelif yükseltgenlerin asıl metallerin yüzeyini oksitlediğini göstermektedir.

Denge değeriine en kısa zamanda ulaşan iridyumdur, onu sra ile rodyum ve platin izlemektedir, (Termodynamik soyluk sırası).
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