Hydrolysis of Rhenium (v) Dioxo Complexes

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Abstract

Electronic spectra and kinetic studies of the hydrolysis of trans-[O₂Re(L)₂]X complexes, where (X=Cl, Br; L=3-, 4-amino pyridine; 3- 4- methyl pyridine) in different acidic media were carried out spectrophotometrically at (λmax=300-330nm) wavelength, showed that the complexes are fairly unstable and their hydrolysis displayed first order reaction, and [ReO₄]⁻ was detected as a final product in the hydrolysis process.

Introduction

The importance of higher oxidation state of oxo complexes of (Ru, Os, Re, Mn, Cr) in oxidation reaction of organic compounds are well known[1-2]. Many metal-oxo reagent with high oxidation state are commonly used in organic synthesis, the mechanisms of their reaction have been examined both experimentally and theoretically, in addition metal oxides and mixed metal oxides were used in catalytic oxidations and the oxo species were suspected in biochemical oxygenase reaction, and in multielectron electrochemical behavior. Kinetic studies of Re (V)-oxo complexes in different media were reported. These studies were used to manipulate reactivity systematically with various ligand[3]. trans-Tetra Kis (pyridine) dioxo rhenium complexes have attracted considerable attention on account of the redox catalytic activity[4-5]. In this paper the electronic spectra and kinetic studies of the trans-[O₂Re(L)₂]X complexes, where (X=Cl, Br; L=3-, 4-amino pyridine; 3- 4- methyl pyridine) in different acidic media are described.

Experimental part

Instrument:-

Spectrophotometer of pye Unicam UV-8700 was used for measuring and recording the absorption bands. pH measurements were made using Phillips pH-meter (PW526).

Materials:-

Triphenyl phosphine, 3-Picoline, 4-Picoline, acetone, hydrochloric acid, sulphuric acid and hydrobromic acid obtained from B.D.H., and 3-amino pyridine and 4-amino pyridine obtained from Aldrich chemical inc, rhenium metal obtained from Merck and NH₄ReO₄ obtained from Johnson Matthey GmbH.

Preparation:-

Literature procedures were used to prepare the complexes of trans-[O₂Re(L)₂]X complexes, where (X=Cl, Br; L=3-, 4-amino pyridine; 3- 4- methyl pyridine). [ReOX₃(PPh₃)₂][7] was used as a starting material while reaction with pyridine derivatives were carried out in acetone under reflux. A kinetic studies in different acidicedia.

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ranges from pH(1.7-6.5), and the complexes' concentration range from $(2.5 \times 10^{-4}$ to $0.06 \times 10^{-4}$)M. Table (1)).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Concentration /Mx10 -4 in aqueous acidic solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans- [OsRe(4-Pic)4]Br</td>
<td>1.20, 1.074, 0.82, 0.32, 0.13</td>
</tr>
<tr>
<td>trans- [OsRe(4-Pic)4]Cl</td>
<td>1.20, 1.074, 0.82, 0.32, 0.13</td>
</tr>
<tr>
<td>trans- [OsRe(4-Pic)4]Cl</td>
<td>1.26, 0.631, 0.315, 0.157, 0.078</td>
</tr>
<tr>
<td>trans- [OsRe(4-Pic)4]CI</td>
<td>1.26, 0.631, 0.315, 0.157, 0.078</td>
</tr>
<tr>
<td>trans- [OsRe(4-Pic)4]Cl</td>
<td>2.5, 1.25, 0.625, 0.2125, 0.154</td>
</tr>
<tr>
<td>trans- [OsRe(4-Pic)4]Cl</td>
<td>2.5, 1.25, 0.625, 0.2125, 0.154</td>
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</tbody>
</table>

Table (1): Complex Concentration /Mx10 -4 in aqueous acidic Solution (H2SO4) *(Pic: methyl pyridine , amy: amino pyridine)

**Result and Discussion**

The maximum absorption bands were spectrophoto-meterically determined for a series of dioxo Rhenium (V) complexes, they showed that best absorption wavelengths were the absorption wavelengths were due to the change transfere which belong to Between (300-300 nm) at different concentrations of the complexes and at different pH Values as indicated in Table (2)

![UV Spectra for trans- [H2O(4-Pic)4]ReV](image)

A study of the hydrolysis of the complexes in different acidic media was
carried out through measurement of the maximum absorption at different times. It was found that hydrolysis of these complexes decreased when the medium acidity increased as shown in figure {2, 3} since substituted ligands were removed out from coordination sphere sufficient protons were provided from the medium to react with ligands through (N) atom which is coordinated with the metal, and consequently enhances the removal of ligands in the form of $H^+ N^- \text{R}^{10-11}$ where $R=3,4$-methyl; 3-,4-amino. The oxidation to Re (VII) of the complexes causing the formation of the oxide ReO$_4^{12-13}$ as a final product was then studied by comparison of UV absorption bands of standard NH$_4$ReO$_4$ solution with ReO$_4$, the product of hydrolysis as shown in figure {4}.

Figure (2) hydrolysis process for trans-\([\text{O}_2\text{Re}(4-\text{Pico})_4]\) in different acidic media
A: in pH 6.5, B: in pH 5.4, C: in pH 2.75, D: in pH 1.7

Figure (3) hydrolysis for complexes in pH 6.5
A: trans-\([\text{O}_2\text{Re}(4-\text{Pico})_4]\), B: trans-\([\text{O}_2\text{Re}(4-\text{Pico})_4]\), C: trans-\([\text{O}_2\text{Re}(4-\text{Pico})_4]\), D: trans-\([\text{O}_2\text{Re}(3-\text{Pico})_4]\), E: trans-\([\text{O}_2\text{Re}(4-\text{ampy})_4]\), F: trans-\([\text{O}_2\text{Re}(4-\text{ampy})_4]\), G: trans-\([\text{O}_2\text{Re}(3-\text{ampy})_4]\), H: trans-\([\text{O}_2\text{Re}(3-\text{ampy})_4]\)

The hydrolysis process of the complexes in different acidic media were of first order with respect to complexes$^{14}$, as it is shown in figure {5}. The effect of increasing concentration of $H_2SO_4$ acid on the rate of reaction has been studied, our results show that the rate of reaction is increasing by increasing the concentration of $H_2SO_4$ acid. It was found that the reaction is fractional order with respect to $H_2SO_4$ acid. Relationship between Log kep and Log $H_2SO_4$ where Log kep denotes the first order rate constant complexes concentration, the slope of the line denotes the order of reaction w.r.t $H_2SO_4$ found that the slope=0.82$^{13}$ in figure {6}. 

297
and the half-life periods of hydrolysis of complexes were obtained from figure (5), from these values it becomes obvious that the rate of hydrolysis increases with increasing the acidity of the medium.

Also table (3) indicated that the rate of hydrolysis when pyridine ligands are the substituted amine at the para-position having higher rate when comparison is made with its meta-substituted complexes. On the other hand when the amine group are substituted by another group such as methyl group in the para or meta position the rate of hydrolysis was found to decrease. However, an approximate rate constant (K1) for the conversion of trans-[O3ReCl3(4-pic)].X to [ReO4] reaction obtained in (H2SO4) medium at pH range (1.7-6.5) and at room temperature. Could be explained according to the following mechanism:

<table>
<thead>
<tr>
<th>Table (3)</th>
<th>Rate constants, half-life periods and order of reaction w.r.t complexes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex</td>
<td>Rate Constant (kl/o10^4 M^-1 s^-1)</td>
</tr>
<tr>
<td>trans-[O3ReCl3(4-pic)].HCl</td>
<td>1.774 (5.5)</td>
</tr>
<tr>
<td>trans-[O3ReCl3(4-pic)].HBr</td>
<td>2.475 (6.5)</td>
</tr>
<tr>
<td>trans-[O3ReCl3(4-pic)].EtOH</td>
<td>3.965 (5.6)</td>
</tr>
<tr>
<td>trans-[O3ReCl3(4-pic)].MeOH</td>
<td>2.841 (6.7)</td>
</tr>
<tr>
<td>trans-[O3ReCl3(4-pic)].PhOH</td>
<td>2.841 (6.7)</td>
</tr>
</tbody>
</table>

Where Log K<sub>acq</sub> denotes the first order rate constant complex Trans-[O3ReCl3(4-Pic)].X concentration, the slope of the line denotes the order of reaction w.r.t H2SO4. |
References


تحلل مائي لمعقدات رينيوم الخماسي ثنائي الأوكسو

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الخلاصة

قدت دراسة حركة وتحلل المعقدات trans-[O₂ReL₂]X بخلاف الكوار أو البروم حيث أن X = -3- أو -4- - مثيل بربين أو -و - ميثيل بربين . بأستخدام حمضية متعددة من حمض الكربيتاك باستخدام مطيافية الأشعة فوق البنفسجية عند طول موجي ضمن مدى (300-700) أوم . ووضحت الدراسة الحركة أن تفاعل التحلل للمعادن من المرتبة الأولى عند تراكيز مختلفة من المعقد وتركيز ثابت من الحمض . كما تم دراسة تأثير زيادة تركيز حمض الكربيتاك على سرعة التفاعل وأوضحت النتائج أن سرعة التفاعل تزداد بزيادة تركيز الحمض حيث وجد أن تفاعل من المرتبة الكسرية بالنسبة إلى حمض الكربيتاك . وأن النتائج النهائية لتفاعل المعقدات هو تكوين أيون الكربيتات .
