Hydrolysis of Rhenium (v) Dioxo Complexes

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Abstract

Electronic spectra and kinetic studies of the hydrolysis of *trans*-[$O_2Re(L)_4$]X complexes ,where (X=Cl ,Br ; L=3-, 4-amino pyridine ;3- 4- methyl pyridine) in different acidic media,were carried out spectrophotometrically at (λ_{max}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.

Introdaction

The importance of higher oxidation state of oxo complexes of (Ru, Os , Re , Mn , Cr) in oxidation reaction of organic compounds are well know[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] . *tans*-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*-[$O_2Re(L)_4$]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 Philips 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- amion pyridine obtained from Aldrich chemical inc ,rhenium metal obtained from Merk and NH_4ReO_4 obtained from Johnson Matthay Gmbh .

Perparation :-

Literature procedures were used to prepare the complexes of *trans*-[$O_2Re(L)_4$]X[6] complexes ,where (X=Cl ,Br ; L=3-, 4-amino pyridine ;3- 4- methyl pyridine). [$ReOX_3(PPh_3)_2$][7] was used as a starting material while reaction with pyridine derivatives were carried out in acetone under refluxe . A kinetic studies in different acidic media

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ranges from pH(1.7-6.5), and the complexes concentration range from (2.5x10^{-4} to 0.06x10^{-4}M). Table ((1)).

Table ((1)):- Complex Concentration /Mx10^{-4} in aqueous acidic Solution (H$_2$SO$_4$)
*Pic : methyl pyridine , ampy : amino pyridine

Complexe	Concentration /Mx10^{-4} in aqueous acid solution
trans-[O$_2$Re(4-Pico)$_4$]Cl	2.09, 1.074, 0.52, 0.2, 0.13 pH(6.5) 2.09 pH(5.4) 2.09 pH(2.75) 2.09 pH(1.7)
trans-[O$_2$Re(4-Pico)$_4$]Br	1.26, 0.631, 0.315, 0.157, 0.078 pH(6.5) 1.26 pH(5.4) 1.26 pH(2.75) 1.26 pH(1.7)
trans-[O$_2$Re(3-Pico)$_4$]Cl	2.5, 1.25, 0.625, 0.3125, 0.156 pH(6.5) 2.5 pH(5.4) 2.5 pH(2.75) 2.5 pH(1.7)
trans-[O$_2$Re(3-Pico)$_4$]Br	1.718, 0.859, 0.429, 0.214, 0.107 pH(6.5) 1.718 pH(5.4) 1.718 pH(2.75) 1.718 pH(1.7)
trans-[O$_2$Re(4-ampy)$_4$]Br	0.66, 0.48, 0.15, 0.1, 0.06 pH(6.5) 0.66 pH(5.4) 0.66 pH(2.75) 0.66 pH(1.7)
trans-[O$_2$Re(4-ampy)$_4$]Cl	0.608, 0.437, 0.314, 0.226, 0.162 pH(6.5) 0.608 pH(5.40 0.608 pH(2.75) 0.608 pH(1.7)
trans-[O$_2$Re(3-ampy)$_4$]Cl	0.55, 0.39, 0.285, 0.205, 0.147 pH(6.5) 0.55 pH(5.4) 0.55 pH(2.75) 0.55 pH(1.7)
trans-[O$_2$Re(3-ampy)$_4$]Br	0.825, 0.594, 0.427, 0.307, 0.221 pH(6.5) 0.825 pH(5.4) 0.825 pH(2.75) 0.825 pH(1.7)

Result and Discussion

The maximum absorption bands were spectrophoto-meterically determine for aseries of dioxo Rhenium (V) complexes, they showed that best absorption wavelengths were The absorption wavelengths were due to the charge transfere which belong to Between (300-300 nm) at different concentrations of the complexes and at different pH Values as indicated in table (2) the following transitions (d π Re (V) → π*(L)) [8-9] see figure {1} .

Table ((2)):- UV Data for Dioxo rhenium (V) Complexes

Re(V)Complex	Solvent	$\lambda_{max,nm}$(CM^{-1}Cm^{-1})
trans-[O$_2$Re(4-Pico)$_4$]$^+$	1x10^{-5} MH$_2$SO$_4$ pH 6.5 1x10^{-4} pH 5.4 1x10^{-3} pH 2.75 1x10^{-2} pH 1.7	245(40816) 330(30303)
trans-[O$_2$Re(3-Pico)$_4$]$^+$	1x10^{-5} MH$_2$SO$_4$ pH 6.5 1x10^{-4} pH 5.4 1x10^{-3} pH 2.75 1x10^{-2} pH 1.7	248(40322) 320(31250)
trans-[O$_2$Re(4-ampy)$_4$]$^+$	1x10^{-5} MH$_2$SO$_4$ pH 6.5 1x10^{-4} pH 5.4 1x10^{-3} pH 2.75 1x10^{-2} pH 1.7	256(39062) 300(33333)
trans-[O$_2$Re(3-ampy)$_4$]$^+$	1x10^{-5} MH$_2$SO$_4$ pH 6.5 1x10^{-4} pH 5.4 1x10^{-3} pH 2.75 1x10^{-2} pH 1.7	253(39525) 330(30303)

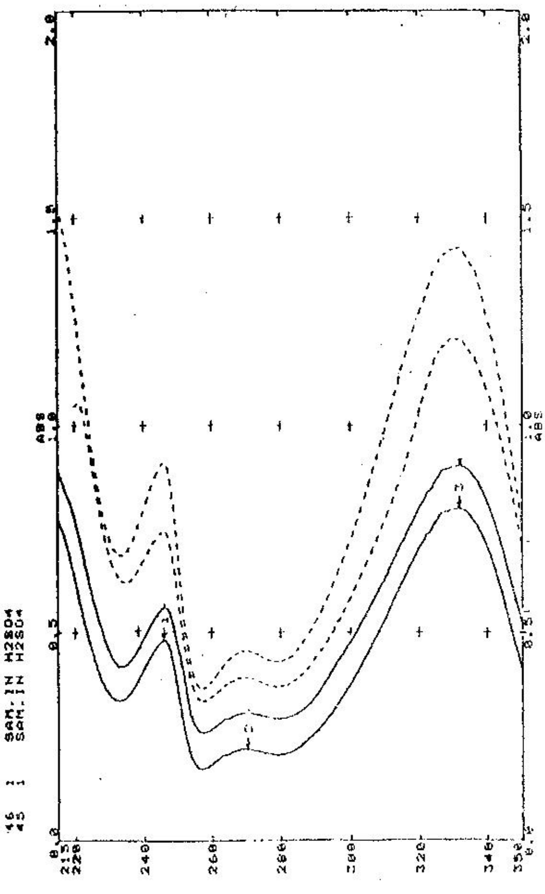


Figure (1). UV- Spectra for trans- [O$_2$Re(4-Pic)$_4$]$^+$
A in 1x10^{-5} H$_2$SO$_4$; B in 1x10^{-4} H$_2$SO$_4$
C in 1x10^{-3} H$_2$SO$_4$; D in 1x10^{-2} H$_2$SO

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 the coordination sphere sufficient protons were provided from the media to react with ligands through (N) atom which is coordinated with the metal , and consequently enhances the removd of ligands in the from of H^+N ? $_R$ [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_4ReO_4 solution with ReO_4^- the product of hydrolysis as shown in figure {4} .

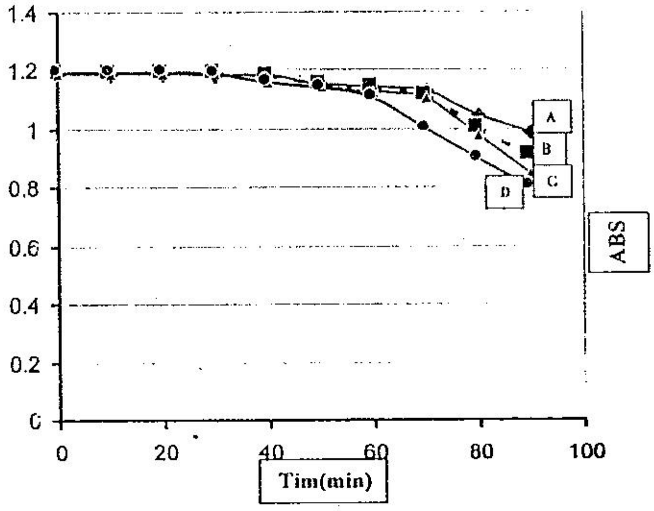


Figure (2) hydrolysis process for trans-$[O_2Re(4\text{-}Pico)_4]^+$ in different acidic media
A: in pH 6.5, B: in pH 5.4, C: in pH 2.75, D: in pH 1.7

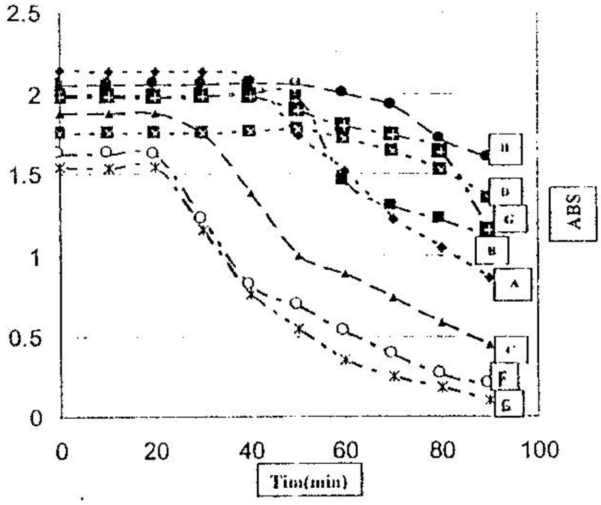


Figure (3) hydrolysis for complexes in pH 6.5 .
A: trans-$[O_2Re(4\text{-}Pico)_4]cl$ B: trans-$[O_2Re(4\text{-}Pico)_4]Br$
C: trans-$[O_2Re(3\text{-}Pico)_4]cl$ D: trans-$[O_2Re(3\text{-}Pico)_4]Br$
E: trans-$[O_2Re(4\text{-}ampy)_4]cl$ F: trans-$[O_2Re(4\text{-}ampy)_4]Br$
G: trans-$[O_2Re(3\text{-}ampy)_4]cl$ H: trans-$[O_2Re(3\text{-}ampy)_4]Br$

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 reat 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 kexp and Log H_2SO_4 where Log kexp denotes the first order rate constant complexes concentration .the slop of the line denoten the order of reaction w.r.t H_2SO_4 found that the slop=0.82 [15] figure {6}.

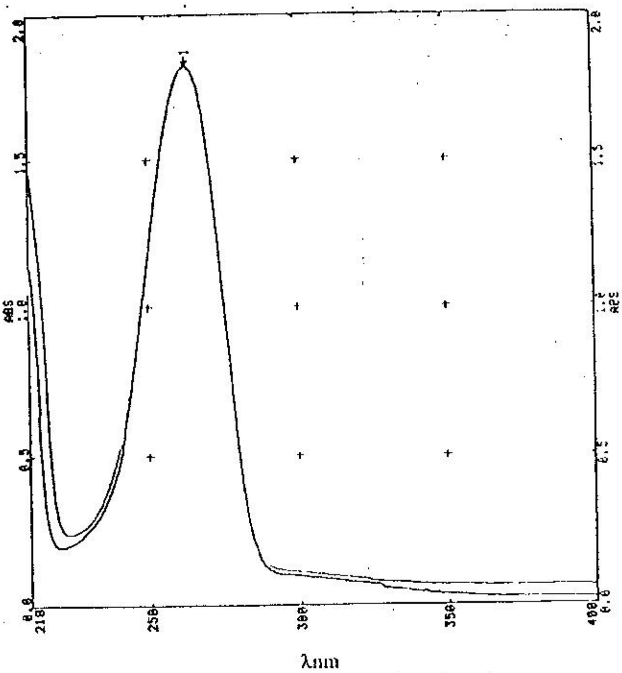
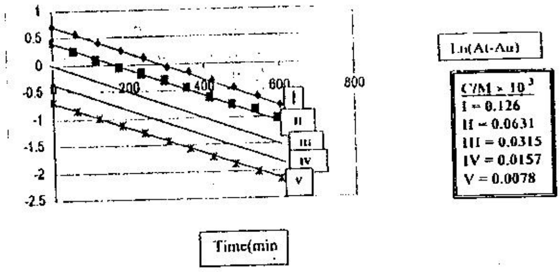


Figure (4): UV- Spectra for hydrolysis product of trans complexes and standard NH_4ReO_4 Solution



Figure(5): graphical relation ship to find the rate of first order reaction of complex trans-$[O_2Re(3\text{-ampy})_4]$ hydrolysis at different concentration and at acidity of 1×10^{-5} M (pH=6.5) in H_2SO_4.

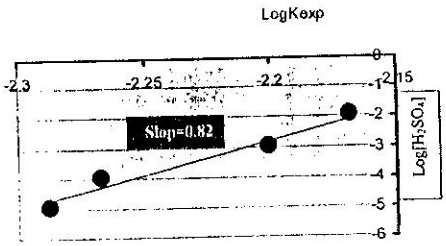


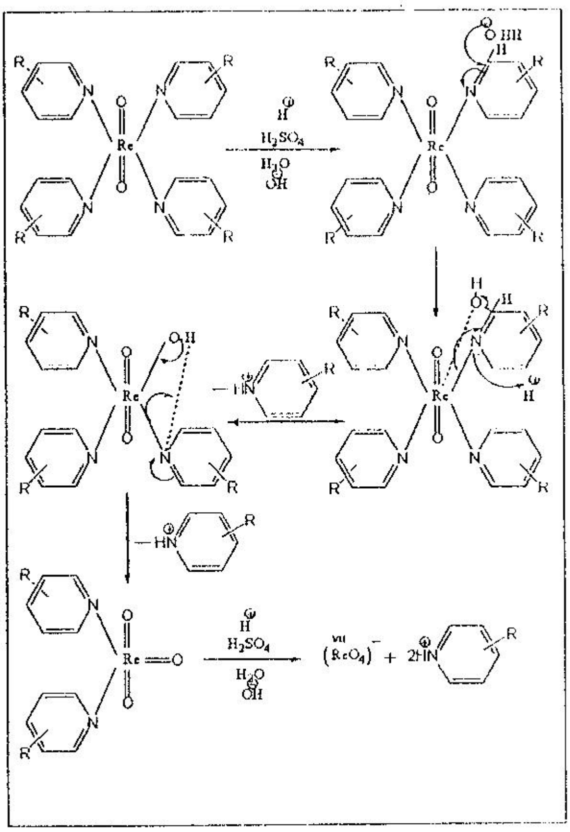
Figure (6): Relationship between Log Kexp and Log $[H_2SO_4]$ Where Log Kexp denotes the first order rate constant complex Trans-$[O_2Re(4\text{-Pico})_4]$cl concentration . the slope of the line denoten the order of reaction w.r.t H_2SO_4.

and the half lift 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 paraposition 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 he rate of hydrolysis was found to decrease ,However, an approximate rate constant (K1) for the conversion of *trans*-$[O_2Re(L)_4]X$ to $[ReO_4]^-$ reaction obtained in (H_2SO_4) medium at pH rang (1.7-6.5) and at room temperature . Could be explained according to the following mechanism:-

Table ((3)):- Rate constants, half- life periods and order of reaction w.r.t complexes .

Complex	RateConstant at different pHvalues K(min)$^{-1}$x10^{-3}(pH)	Half-Life $t_{1/2}$	Order of reaction w.r.t complexes
trans-$[O_2Re(4\text{-Pico})_4]$cl	5.164 (6.5) 5.414 (5.46) 6.3 (2.75) 5.165 (1.7)	134 128 110 102	first
trans-$[O_2Re(4\text{-Pico})_4]$Br	2.83 (6.5) 2.987 (5.46) 3.223 (2.75) 5.166 (1.7)	244.8 232 215 200	first
trans-$[O_2Re(3\text{-Pico})_4]$cl	2.84 (6.5) 4.589 (5.4) 5.25 (2.75) 5.544 (1.7)	160 151 132 125	first
trans-$[O_2Re(3\text{-Pico})_4]$Br	2.665 (6.5) 2.794 (5.4) 2.987 (2.75) 3.135 (1.7)	260 248 232 221	first
trans-$[O_2Re(4\text{-ampy})_4]$cl	8.662 (6.5) 9.364 (5.4) 10.992 (2.75) 12.375 (1.7)	80 74 68 56	first
trans-$[O_2Re(4\text{-ampy})_4]$Br	7.875 (6.5) 9.772 (5.4) 10.343 (2.75) 11.177 (1.7)	88 79 67 62	first
trans-$[O_2Re(3\text{-ampy})_4]$cl	2.475 (6.5) 2.565 (5.4) 2.728 (2.75) 2.783 (1.7)	280 268 254 249	first
trans-$[O_2Re(3\text{-ampy})_4]$Br	2.165 (6.5) 2.264 (5.4) 2.325 (2.75) 2.397 (1.7)	320 306 298 289	first



Hydrolysis scheme of $[O_2Re(L)_4]^+$ complexes
R= 3- , 4 methy ; 3-, 4- amine

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تحلل مائي لمعقدات رينيوم الخماسي ثنائي الاوكسو

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الخلاصة

تمت دراسة حركية وتحلل للمعقدات *trans*-$[O_2Re(L)_4]X$ حيث أن(X يمثل الكلور او البروم L يمثل ٣- أو ٤- مثيل بردين أو ٣- أو ٤- أمينو بردين) . بأوساط حامضية متعددة من حامض الكبريتيك باستخدام مطيافية الأشعة فوق البنفسجية عند طول موجي ضمن مدى (٣٠٠-٣٣٠نم) أوضحت الدراسة الحركية أن تفاعل التحلل للمعقدات من المرتبة الاولى عند تراكيز مختلفة من المعقد وتركيز ثابت من الحامض .كما تم دراسة تاثير زيادة تركيز حامض الكبريتيك على سرعة التفاعل وأوضحت النتائج أن سرعة التفاعل تزداد بزيادة تركيز الحامض حيث وجد أن التفاعل من المرتبة الكسرية بالنسبة الى حامض الكبريتيك. وأن الناتج النهائي لتحلل المعقدات هو تكوين ايون البرينيت.