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Rhenium Part XI. Mixed Ligand Complexes of Tetra- and Quinquevalent Rhenium Containing Pyridine and Bromide or Iodide

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Nonelectrolytic complexes $[ReO(OH)py_2X_2]$ *(X = Br and I) have been isolated by the action of cold dilute HX on* $[ReO_2py_4]Br\cdot 2H_2O$ *and* $[ReO_2py_4]I\cdot H_2O$. *Hot and concentrated HBr produced* $[ReOpy_2Br_3]$ *and* $(pyH)_2[ReBr_6]$ *with* $[ReO_2py_4]Br\cdot 2H_2O$ *whereas hot and concentrated HI gave* $[Repy_2I_4]$ *with* $[ReO_2py_4]I\cdot H_2O$. *The thermal decomposition of* $[ReO_2py_4]Br\cdot 2H_2O$ *and* $[ReO_2py_4]I\cdot H_2O$ *has been studied by thermogravimetry and the compound* $Re_2O_7py_2$ *has been isolated by isothermal heating of both the bromo and iodo salts. Molecular conductivities, magnetic susceptibility and i.r. spectra have been reported.*

Introduction

Quinquevalent rhenium forms a large number of stable diamagnetic or very weakly paramagnetic complexes in which the metal forms multiple bonds to oxygen. They are mostly octahedral and are of the types $[ReOX_5]^{2-}$, $[ReOX_4L]^-$, $[ReOX_3L_2]$, $[ReO_2X_4]^{3-}$, $[ReO_2L_4]^+$ and $(ReOX_2L_2)_2O$[1]. The most thoroughly studied cationic oxo complex[2–4] of Re(V) is $[ReO_2py_4]^+$. One of us has previously investigated the behaviour of $[ReO_2py_4]Cl$ towards HCl and observed[2] that with cold dilute and hot strong HCl the nonelectrolytic complexes $[ReO(OH)py_2Cl_2]$ and $[ReOpy_2Cl_3]$ respectively are obtained. This has settled the differences of opinion regarding the nature of the product obtained in the hot condition which was variously formulated as $[ReO_2py_4]_2[ReOCl_5]$, $[ReO(OH)py_4][ReOCl_5]$ and $[Re(OH)_2py_2Cl_2]Cl$[3–5]. We have also previously studied the thermal decomposition of $[ReO_2py_4]Cl\cdot 2H_2O$ and isolated two compounds, *viz.*, $Re_2O_3py_4Cl_4$ and $Re_2O_7py_2$ from the pyrolysis product[2]. In the present communication we have extended these studies with the salts $[ReO_2py_4]Br\cdot 2H_2O$ and $[ReO_2py_4]I\cdot H_2O$ with the object of comparing the behaviour of the salts $[ReO_2py_4]X$ towards HX and heat. Due to the reducing character of HBr and HI, the bromide and particularly the iodide salts are expected to react in a different manner compared with the chloride.

Experimental

Potassium perrhenate used was of Degussa (West Germany). Potassium bromide and potassium iodide were E. Merck's guaranteed reagents. Hydrobromic acid (40%), hydriodic acid (55%) and pyridine were of B.D.H. A.R. quality. Hydriodic acid was distilled before use[6]. $[ReO_2py_4]Cl\cdot 2H_2O$ was prepared as described earlier[2].

Rhenium was estimated by decomposing the complexes with sodium peroxide and then precipitating rhenium heptasulphide. The precipitate was dissolved in aqueous sodium peroxide and rhenium determined gravimetrically as tetraphenyl arsonium perrhenate[7]. Bromide and iodide were estimated gravimetrically by silver nitrate method after decomposing the samples by boiling with sodium peroxide in water. Nitrogen, carbon and hydrogen were determined by standard microanalytical method.

Conductance and magnetic susceptibility measurements and the recording of i.r. spectra and TGA curves were made by the methods described in our previous communications[2,8].

Preparation of the Complexes

Dioxotetrapyridinerhenium(V) bromide dihydrate $[ReO_2py_4]Br\cdot 2H_2O$ *and dioxotetrapyridinerhenium(V) iodide monohydrate* $[ReO_2py_4]I\cdot H_2O$.

These were prepared by precipitating concentrated solutions of $[ReO_2py_4]Cl\cdot 2H_2O$ (1g) with excess of potassium bromide and iodide respectively. The precipitates were washed with cold water and recrystallised from ethanol. The yields of the products dried over sulphuric acid were 0.7 g.

Oxohydroxodibromodipyridinerhenium(V), $[ReO(OH)py_2Br_2]$ *and oxohydroxodiiododipyridinerhenium(V),* $[ReO(OH)py_2I_2]$

1 g of $[ReO_2py_4]Br\cdot 2H_2O$ (or $[ReO_2py_4]I\cdot H_2O$) was dissolved in 50 ml of 20% HBr (or HI in the latter

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case). The solutions were filtered from a small amount of the residue and the filtrates were kept for 48 hours with occasional stirring. The precipitates were filtered, washed successively with dilute (about 1*N*) HBr (or HI in the latter case) and acetone (ethanol in the case of the iodo complex). The complexes were then dried over sulphuric acid. The yields of the bromo and iodo complexes were 0.6 g and 0.2 g respectively.

Oxotribromodipyridinerhenium(V), [ReOpy₂Br₃]

1 g of $[ReO_2py_4]Br \cdot 2H_2O$ was dissolved in 10 ml 40% HBr. The red solution was boiled for about half an hour when a green precipitate appeared. This was separated when still hot by centrifugation and the red mother liquor was preserved. The precipitate was washed with dilute (about 1*N*) HBr and then with acetone. It was dried over sulphuric acid. The yield was 0.5 g.

Pyridinium hexabromorhenate(IV), $(pyH)_2$ $[ReBr_6]$

The mother liquor after separation of $[ReOpy_2Br_3]$ was concentrated by boiling for about half an hour and then allowed to cool when orange red crystals appeared. These were separated and washed twice with concentrated HBr and then with acetone four times. The yield of the complex dried over sulphuric acid was about 0.2 g.

Tetraiododipyridinerhenium(IV), $[Repy_2I_4]$

0.3 g of $[ReO_2py_4]I \cdot H_2O$ was refluxed with 15 ml freshly distilled HI (sp. gr. 1.70) for one hour. The mixture was cooled and filtered and the residue was washed successively with HI (about 1*N*), ethanol and acetone. It was dried over sulphuric acid and the yield was 0.35 g.

$Re_2O_7py_2$

This was obtained by heating $[ReO_2py_4]Br \cdot 2H_2O$ to constant weight at 155° C. The colour slowly changed from orange yellow to green, greenish brown and finally light brown. The loss in weight was 50.3% which was attained in about 100 hours. This compound was also obtained on heating $[ReO_2py_4]I \cdot H_2O$ at 135° C. The loss was 52.12%.

Results and Discussion

Like dioxotetrapyridinerhenium(V) chloride, both $[ReO_2py_4]Br$ and $[ReO_2py_4]I$ react with cold dilute HBr and HI respectively to give the nonelectrolytic complexes $[ReO(OH)py_2X_2]$. Hot concentrated HBr brings about partial reduction of Re(V) in $[ReO_2py_4]Br$ and gives two products, *viz.*, $[ReOpy_2Br_3]$ (insoluble in HBr) and $(pyH)_2$ $[ReBr_6]$ (soluble in hot HBr) containing Re(V) and Re(IV) respectively. With $[ReO_2py_4]Cl$, under similar conditions, only $[ReOpy_2Cl_3]$ is obtained[2]. Hot concentrated HI effects complete reduction of Re(V) in $[ReO_2py_4]I$ and produces a nonelectrolytic complex $[Repy_2I_4]$. This compound has been reported previously and was prepared from ReI_4 and pyridine in acetone medium[9, 10].

Both the complexes $[ReO(OH)py_2X_2]$ (X = Br and I) are insoluble in water. The bromo complex is also insoluble in ethanol, methanol and acetone, but moderately soluble in nitrobenzene. The iodo complex is sparingly soluble in ethanol and fairly soluble in acetone and nitrobenzene. $[ReOpy_2Br_3]$ and $[Repy_2I_4]$ are insoluble in water and common organic solvents. The hexabromo complex, $(pyH)_2$ $[ReBr_6]$ is soluble in water and the solution deposits rhenium dioxide on warming.

The molecular conductance of an $1 \times 10^{-3}M$ nitrobenzene solution of the bromo complex $[ReO(OH)py_2Br_2]$ was 6.1 ohm^{-1} at 25°C, while that of the analogous iodo complex (acetone solution of the same concentration) was 43.5 ohm^{-1} at 25° C. These values are lower than expected even for an 1:1 electrolyte. The complexes are thus nonelectrolytic ones, which, however, undergo dissociation to some extent in highly dilute solutions.

The quinquevalent oxo complexes of rhenium are very weakly paramagnetic (vide Table II) which agrees with the similar properties of other Re(V) oxo complexes reported earlier[8, 11]. The tetravalent complexes are however, as expected,[11] paramagnetic with magnetic moments slightly lower than the spin-only value for three unpaired electrons (vide Table II).

The i.r. spectra of $[ReO(OH)py_2Br_2]$ and $[ReO(OH)py_2I_2]$ are very similar to that of $[ReO(OH)py_2Cl_2]$ (green form)[2] and show strong $\nu(Re{=}O)$ bands around 975 cm^{-1} (*vide* Table II). $\nu(O{-}H)$ band is absent (as observed earlier also)[2, 12] in the spectra of all these three complexes, $[ReO(OH)py_2X_2]$. The spectra of the two oxo complexes $[ReOpy_2X_3]$ (X = Cl and Br) are also very similar (Table II)[2]. $\nu(Re{=}O)$ in these complexes appears as strong bands around 970 cm^{-1}. In the spectra of any of these oxo or hydroxo complexes no strong band in the region 900–780 cm^{-1} is present which indicates the absence of bridging Re=O group.

The TGA curves of both the salts $[ReO_2py_4]Br \cdot 2H_2O$ and $[ReO_2py_4]I \cdot H_2O$ indicate that they begin to decompose above 50° C. As in the case of the chloride salt[2], the loss of water and pyridine takes place simultaneously with these two salts also. The TGA curves of the bromide and the iodide salts gave weak horizontals around 100° C and the losses correspond approximately to the removal of water. The curve for the bromide salt gave a horizontal between 200–230° C with a loss of about 40% which is slightly higher than that calculated on the basis of the following equation (calc. 34.7%):

TABLE I. Analytical Data[a] and Colour of the Complexes.

Complexes and Their Colour	% Re	% Br or I	% C	% H	% N
$[ReO_2py_4]Br \cdot 2H_2O$	27.75	12.49	38.34	3.32	
Orange yellow	(28.62)	(12.29)	(36.93)	(3.72)	
$[ReO_2py_4]I \cdot H_2O$	27.47	19.56	35.89	3.42	8.36
Orange yellow	(27.40)	(18.67)	(35.34)	(3.26)	(8.25)
$[ReO(OH)py_2Br_2]$	34.92	30.29	22.51	2.09	5.33
Green	(34.66)	(29.74)	(22.35)	(2.06)	(5.22)
$[ReOpy_2Br_3]$	31.02	40.06	20.39	1.60	4.81
Light green	(31.03)	(39.94)	(20.01)	(1.68)	(4.67)
$(pyH)_2[ReBr_6]$	22.03	57.88	14.76	1.45	3.75
Orange red	(22.55)	(58.04)	(14.54)	(1.47)	(3.39)
$[ReO(OH)py_2I_2]$	29.20	41.03			4.30
Light brown	(29.51)	(40.22)			(4.44)
$[Repy_2I_4]$	22.13	59.72	14.30	1.35	
Deep violet	(21.86)	(59.57)	(14.10)	(1.18)	
$Re_2O_7py_2$	57.08		19.35	2.19	3.92
Light brown	(57.95)		(18.69)	(1.57)	(4.36)

[a] The values in parenthesis are the calculated ones.

TABLE II. Magnetic Susceptibility and I.r. Spectral Bands of the Complexes (in nujol mull).

Complex	$\chi_M \times 10^6$ c.g.s. units	$\chi_M' \times 10^6$ c.g.s. units	μ_{eff} BM at 35 °C	ν(cm^{-1})	
				ν(Re=O)	Other Bands
$[ReO_2py_4]Br \cdot 2H_2O$	−239.6	31.0	0.28		
$[ReO_2py_4]I \cdot H_2O$	−233.6	40.0	0.32		
$(pyH)_2[ReBr_6]$	5368	5674	3.76		
$[ReO(OH)py_2Br_2]$	−104.6	81.6	0.45	980s	1615s, 1250m, 1225s, 1160s, 1070s, 1055s, 1020w, 955w, 920mbr, 770s, 765s, 720s (overlapped with nujol band), 695s, 670s, 645s
$[ReOpy_2Br_3]$	−76.6	132.2	0.57	965vs	1610m, 1215s, 1150wbr, 1065s, 1015w, 935w, 755vs, 680s
$[ReO(OH)py_2I_2]$				970s	1615s, 1220w, 1155m, 1070s, 1050sh, 1045s, 1010s, 915m, 810w, 760s, 690vs, 665vs, 645sh, 630vs
$[Repy_2I_4]$	4897	5197	3.59		
$Re_2O_7py_2$				970m, 910vs, 880s	1640w, 1610s, 1535s, 1260w, 1250w, 1210w, 1175m, 1060w, 1035w, 750s, 680s, 610w
$[ReO(OH)py_2Cl_2]$[a] Green Form				980s	1615s, 1380w, 1218m, 1165w, 1070m, 1053m, 765s, 755vs, 697w, 688m, 676m, 644w

[a] Spectral data taken from ref. 2 for comparison.

$$4[ReO_2py_4]Br \cdot 2H_2O + O_2 \rightarrow Re_2O_3py_4Br_4 + Re_2O_7py_2 + 10py + 8H_2O$$

The chloride salt $[ReO_2py_4]Cl \cdot 2H_2O$ has been previously shown to decompose in this manner[2]. The pyrolysis curve of $[ReO_2py_4]I \cdot H_2O$ gave very weak horizontals around 180° and 300° C with losses of about 35 and 65% respectively. The loss at 180° C is close to the value of 30.6% calculated on the basis of the above equation (with I in place of Br).

Isothermal heating of $[ReO_2py_4]Br \cdot 2H_2O$ and $[ReO_2py_4]I \cdot H_2O$ at 155° and 135° C respectively gave losses of 50.3 and 52.1% respectively which correspond to the formation of $Re_2O_7py_2$ as follows:

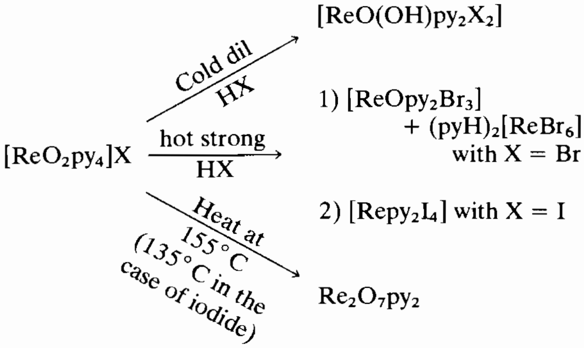
$$2[ReO_2py_4]X \cdot nH_2O + O_2 \rightarrow Re_2O_7py_2 + 2HX + 6py + (2n{-}1)H_2O$$

The calculated losses according to the above equation are 50.6 and 52.7% respectively for the bromide and iodide.

The analysis of the pyrolysis product in both the cases agrees with the composition $Re_2O_7py_2$. The absence of $Re_2O_3py_4X_4$ (X = Br and I) in the pyrolysis product may be due to the weak thermal stability of $Re_2O_3py_4Br_4$ and $Re_2O_3py_4I_4$ compared to $Re_2O_3py_4Cl_4$. The latter could be isolated by heating $[ReO_2py_4]Cl \cdot 2H_2O$[2].

$Re_2O_7py_2$ prepared from the bromide and iodide salts is light brown and soluble in ethanol and acetone. The product obtained by the pyrolysis of $[ReO_2py_4]Cl \cdot 2H_2O$ is however, violet and insoluble in ethanol. This difference is probably due to the different extent of polymerisation in the products. The molecular conductivity of an acetone solution ($1X10^{-3}M$) of $Re_2O_7py_2$ (light brown form) is 12.0 ohm^{-1} at 25° C indicating its nonelectrolytic nature. The i.r. spectra (Table II) of the brown product is very similar to that of the violet complex[2]. Besides the bands due to coordinated pyridine, the spectrum gives strong to medium intensity bands at 970, 910 (very strong and broad) and 880 cm^{-1}. The first two bands may be assigned as due to terminal Re=O vibrations. The δ(Re–O–Re) band may either be overlapped with the strong pyridine band at 750 cm^{-1} or shifted to a higher frequency at 880 cm^{-1}.

The action of heat and hydrohalic acid under different conditions on $[ReO_2py_4]Br \cdot 2H_2O$ and $[ReO_2py_4]I \cdot H_2O$ may thus be represented by the following equations:



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