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Perrhenate-Halide Reactions in Sulphuric Acid: an Alternative Preparation of Rhenium(VI) Tetrabromide Oxide

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Although rhenium(VI) very rapidly disproportionates in aqueous media according to:

$$3\ \mathrm{Re(VI)} \rightarrow 2\ \mathrm{Re(VII)} + \mathrm{Re(IV)}$$

available evidence suggests that this still uncommon oxidation state for rhenium may be more stable in other solvent systems. After our initial work [1] on the preparation of $[ReOCl_5]^-$ from $ReOCl_4$ in chloroform and dichloromethane, other workers [2, 3] showed that salts containing this anion may be prepared by dry hydrogen chloride gas reduction of perrhenate in various organic solvents. Subsequently one of us showed [4] that reduction to rhenium(VI) occurred when an alkali metal bromide was added to a solution of a perrhenate in concentrated sulphuric acid, it being proposed that $ReOBr_4$ was formed in this reaction. A further study [5] indicated that a rapid method for the quantitative estimation of rhenium could be based on this reduction.

We have now explored this reaction with a view to developing a preparative route from $[ReO_4]^-$ to $ReOBr_4$. This compound is a major product of various rhenium oxide-bromine and rhenium bromide-oxygen reactions [6] but species such as ReO_3Br are also formed. Sealed tube reactions between the metal and bromine-sulphur dioxide mixtures at 400 °C also afford $ReOBr_4$ [7].

A preparation in concentrated sulphuric acid, based on the reduction:

$$2\ \mathrm{Re(VII)} + 2\ \mathrm{Br}^- \rightarrow 2\ \mathrm{Re(VI)} + \mathrm{Br_2}$$

has the advantages (a) readily available, stable, perrhenate as starting material, (b) a quantitative and rapid reduction at room temperature, (c) after removal of bromine, $ReOBr_4$ can be quantitatively extracted into an organic solvent and (d) the product will not be subject to hydrolysis or oxidation whilst in contact with the acid. However $ReOBr_4$ is very moisture-sensitive so all subsequent manipulations must be carried out in a vacuum line or an efficient dry-box.

The preparative details are as follows: ammonium perrhenate (0.27 g; 1.0 mmol) is dissolved in 98% H_2SO_4 (20 cm^3) and a 20–50 fold excess of NaBr (*ca.* 3 g) added in small portions with stirring. The solution becomes green-blue and as HBr and Br_2 are evolved a dark blue-black solid is formed. After 20–30 minutes, the solid is extracted into anhydrous toluene (5 × 20 cm^3) and after combining the extracts the toluene is removed by a room temperature distillation in a high vacuum system (*ca.* 25 mtorr) leaving solid $ReOBr_4$ in essentially quantitative yield. The product was subsequently handled under dry nitrogen.

Analysis: Found: Re, 35.7; Br, 61.5%; oxidation state by titration, 6.0. $ReOBr_4$ requires: Re, 35.9 Br, 61.9%.

The preparation can equally well be carried out with an alkali metal perrhenate or a concentrated aqueous solution of perrhenic acid replacing NH_4ReO_4, together with any alkali metal bromide.

The room-temperature magnetic moment, diffuse reflectance visible spectrum and infrared spectrum of $ReOBr_4$ have previously been reported [7], so for additional characterisation we report solution visible, mass and Raman spectra.

The visible spectrum of the product in dry toluene comprises two bands with maxima at 575 and 668 nm, in agreement with previous results [5]. The mass spectrum (recorded at 85 °C on an A.E.I. MS 12 spectrometer using a direct insertion probe with ionising electrons of nominally 70 eV), is similar to that of $ReOCl_4$ [8]. The fragmentation patterns of both compounds are shown in Table I, ion abundances being obtained by summation of the isotope contributions for a particular ion. The ions can be clearly identified by their isotopic distributions resulting from appropriate combinations of ^{185}Re (37.1%), ^{187}Re (62.9%), ^{79}Br (50.5%) and ^{81}Br (49.5%). For example, $ReBr^+$ and $ReOBr^+$ both appear as a pattern of three peaks, each two mass units part, with relative intensities 1:3.0:1.7. No fragments containing two or more metal atoms and no metastable peaks have been observed. Apart from expected fragment ions, ReO_3Br^+, ReO_2Br^+, ReO_3^+ and ReO_2^+ have also been detected with relative abundances 26.2, 9.6, 7.7 and 4.8 respectively. These presumably arise from the volatilization of ReO_3Br generated by oxidation of a little of the $ReOBr_4$ whilst held on the direct insertion probe. We are confident in view of the analytical results and the

TABLE I. Fragmentation Patterns of $ReOX_4$ (X = Cl or Br).

Ion	Relative Abundances	
	$ReOCl_4$ [8]	$ReOBr_4$
$ReOX_4^+$	36.7	30.8
$ReOX_3^+$	100	100
$ReOX_2^+$	25.2	46.2
$ReOX^+$	6.2	15.4
ReO^+	1.9	8.7
ReX_4^+	0.19	*ca.* 0.02
ReX_3^+	4.9	6.7
ReX_2^+	8.4	17.3
ReX^+	6.4	12.5
Re^+	5.2	12.5

absence of ν(ReO) bands of ReO_3Br in the infrared and Raman spectra of the product [9] that this bromide oxide is not present in the initial product. The mass spectrum confirms the existence of $ReOBr_4$ as a discrete monomer in the vapour phase. It is interesting to note that the d^0 five-co-ordinate gaseous molecules $MoOCl_4$, $WOCl_4$ and $WOBr_4$ [8] give spectra in which the parent ions have relative abundances of less than 1%, whereas the parent ions of the d^1 species $ReOCl_4$ and $ReOBr_4$ are present to the extent of at least 30% relative abundance. In all cases the base peak is MOX_3^+.

The infrared spectrum of solid $ReOBr_4$ has bands at 1005 *vs.* ν(ReO), 364 ms δ(OReBr) and 242 s ν(ReBr) cm^{-1}. A Raman spectrum of the solid (514.5 nm excitation; Spex 1401 double monochromator) showed bands at 997 m, 290 mw, 270 s, and 245 s cm^{-1}.

We have also investigated the analogous chloride system in the hope of devising a route to $ReOCl_4$. However reactions in 98% sulphuric acid between aqueous perrhenic acid or a solid alkali metal perrhenate and 11 *M* hydrochloric acid or a solid alkali metal chloride, do not generate chlorine, bright yellow solutions containing only rhenium(VII) being formed. It is probable that the $[ReO_3Cl_3]^{2-}$ ion [10] or a related sulphato-species is formed in these solutions. Attempts to confirm this by Raman spectroscopy have not been successful, the ν(ReO) regions being masked by intense broad bands centred at 1037 [$\nu(SO)_{sym}$, HSO_4^-] and 906 cm^{-1} [(ν(S–OH), HSO_4^- and $\nu(S(OH)_2)_{sym}$, H_2SO_4]. If HCl gas is passed into these solutions for an *extended* period the wine-red colour characteristic of $[ReOCl_5]^-$ very slowly develops.

We conclude that whereas $[ReO_4]^-$ has sufficient oxidising potential in 98% H_2SO_4 to liberate bromide from bromide ion, it is not able to oxidise chloride ion to chlorine and so $ReOCl_4$ cannot be prepared in an analogous manner to $ReOBr_4$ in this solvent.

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