Some Complex Oxyfluorides of Septavalent Rhenium.

By R. D. Peacock.

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Bromine trifluoride reacts with metallic per-rhenates to form complex oxyfluorides of septavalent rhenium, of general formula $M^{I}ReO_2F_4$ and $M^{II}(ReO_2F_4)_2$. Complete substitution of fluorine for oxygen leading to oxygen-free compounds does not take place under the conditions employed.

Although oxyfluoride complexes of molybdenum and tungsten are well known (cf. Sidgwick, " The Chemical Elements and their Compounds," Vol. II, p. 1044) none of rhenium has been described. Ruff and Kwasnik (*Z. anorg. Chem.*, 1934, **219**, 65) and also Wiechert (*ibid.*, 1950, **268**, 310) observed residues containing potassium, rhenium, oxygen, and fluorine, but in neither case was a definite compound isolated. Aynsley, Peacock, and Robinson (*J.*, 1950, 1622), using fluorine itself on potassium per-rhenate, obtained only the two volatile oxyfluorides, rhenium dioxytrifluoride ReO_2F_3 and oxypentafluoride $ReOF_5$, leaving a residue of potassium fluoride. In the present investigation bromine trifluoride has been used as the fluorinating agent (cf. Sharpe, *J.*, 1950, 3444), more particularly in view of the successful preparation of complex fluorides of some of the platinum metals (cf. Hepworth, Peacock, and Robinson, *J.*, 1954, 1197) by this means.

Potassium per-rhenate reacts quietly with bromine trifluoride at room temperature; oxygen and bromine are evolved and warming gives a clear yellow solution which, after the solvent has been pumped off, yields a cream-coloured solid. This is potassium tetrafluoroper-rhenate, $KReO_2F_4$; being very hygroscopic, it can only be kept in a dry atmosphere. Its dissolution in water appears soon to be followed by hydrolysis since the initial yellow colour is soon lost, and the colourless liquid gives the reactions of fluoride, per-rhenate, and potassium ions only: $KReO_2F_4 + 2H_2O \longrightarrow K^+ + 2H^+ + ReO_4^- + 2HF_2^-$. The hydrolysis is greatly accelerated by alkali, which immediately decolorizes the solution.

Replacement of potassium by rubidium, cæsium, silver, or barium per-rhenate yields the corresponding complex fluoro-salts $RbReO_2F_4$, $CeReO_4F_4$, $AgReO_2F_4$, and $Ba(ReO_2F_4)_2$, which have similar properties, although the silver salt is darker.

Calcium and strontium per-rhenates, however, are not completely soluble in bromine trifluoride so that pure complex salts were not obtained; further, the residues contained less rhenium than the values calculated for the fluoro-salts, suggesting that the complexes are solvolysed to some extent in bromine trifluoride solution. Sodium per-rhenate is soluble in bromine trifluoride but the product, even after prolonged drying, still contains bromine. Analysis showed the rhenium content to be low; it is probable that the bromine is present as sodium tetrafluorobromite $NaBrF_4$.

That completely substituted complex fluorides of rhenium are not formed by this method is to be expected; formation of complexes of the type M^IReF_5 as with manganese, or M^IReF_6 as with ruthenium (Hepworth, Peacock, and Robinson, *loc. cit.*), would imply reduction of the stable septavalent state, and no complex salts of the type M^IAF_8 are yet known. The tetrafluoroper-rhenates can be regarded as derivatives of ReO_2F_3 in which the co-ordination number of the rhenium is increased to 6. Other fluorine derivatives of per-rhenates might be expected to exist, *e.g.*, $M^I_2ReO_3F_3$ and $M^I_3ReO_4F_2$, but attempts to prepare one or both of these series by fusion of per-rhenates with potassium hydrogen difluoride, KHF_2, at 250° have been unsuccessful.

EXPERIMENTAL

Metallic per-rhenates were prepared by dissolving powdered rhenium metal in dilute hydrogen peroxide to give per-rhenic acid, neutralizing portions of the hot solution with the corresponding metallic carbonate, and then filtering. Potassium, rubidium, cæsium, and silver per-rhenate separated from their respective solutions on cooling, and sodium and the alkaline-earth per-rhenates crystallized on evaporation of their solutions nearly to dryness. Before reaction the salts were dried at 100° in a vacuum.

Bromine trifluoride was prepared from dry bromine by treating the liquid with hydrogen fluoride-free fluorine suitably diluted with nitrogen, the Pyrex reaction vessel being cooled to 0° in an ice-bath. The crude product was purified by distillation and fractionation in a vacuum.

Potassium per-rhenate reacted immediately with bromine trifluoride at room temperature; the mixture became warm. After evolution of bromine and oxygen had nearly ceased, the remaining solid was dissolved in the bromine trifluoride by warming, and the reaction completed by boiling the solution for 5 min. This solution deposited a quantity of a yellow solid on cooling, which, when the excess of bromine trifluoride had been pumped off at room temperature, appeared as a cream-coloured residue. It was gradually heated to 200° in a vacuum, and after about 30 min. at this temperature, when no more bromine trifluoride could be pumped off, proved to be bromine-free *potassium tetrafluoroper-rhenate* $KReO_2F_4$ (Found: K, 11·9; Re, 55·7; F, 23·0. $KReO_2F_4$ requires K, 11·7; Re, 55·9; F, 23·0%). The ***rubidium, cæsium, silver,*** and ***barium*** salts were prepared in a similar manner [Found: Rb, 22·2; Re, 49·3; F, 18·1. $RbReO_2F_4$ requires Rb, 22·5; Re, 49·1; F, 20·0%. Found: Cs, 31·2; Re, 43·1; F, 18·1. $CsReO_2F_4$ requires Cs, 31·1; Re, 43·6; F, 17·8%. Found: Ag, 26·2; Re, 46·8; F, 18·7. $AgReO_2F_4$ requires Ag, 26·2; Re, 46·3; F, 18·9%. Found: Ba, 18·7; Re, 51·0; F, 21·5. $Ba(ReO_2F_4)_2$ requires Ba, 18·9; Re, 51·3; F, 20·9%].

The calcium and strontium salts were similarly prepared, but the bromine trifluoride solutions were boiled for longer periods in an attempt to bring all the per-rhenate into solution [Found: Re, 55·2; F, 25·3. Calc. for $Ca(ReO_2F_4)_2$: Re, 59·2; F, 24·2%. Found: Re, 56·0; F, 24·0. Calc. for $Sr(ReO_2F_4)_2$: Re, 55·1; F, 22·5%]. In the sodium salt thus prepared, bromine was detected in the residue even after prolonged heating in a vacuum, and its presence in quantity is shown by the observed equivalent weight (Found: Re, 52·1%; equiv., 338. Calc. for $NaReO_2F_4$: Re, 58·7%; equiv., 317·3).

The above materials were analysed, after removal of interfering elements, rhenium as nitron per-rhenate, fluorine as lead chlorofluoride, alkali metals and barium as sulphate, and silver as chloride.

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DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

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