

## 85. Some Hexafluororhenates(v).

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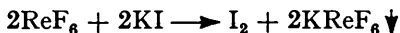
Complex fluorides of rhenium involving the quinquevalent  $\text{ReF}_6^-$  ion have been obtained from the action of potassium iodide on rhenium hexafluoride,  $\text{ReF}_6$ , in liquid sulphur dioxide. Their hydrolysis is described.

THE work of the last few years on the complex fluorides of the platinum metals has stimulated interest in the possibility of making rhenium analogues. Recently quadrivalent complexes of the type  $\text{M}_2\text{ReF}_6$  have been isolated,<sup>1,2</sup> but so far the quinquevalent series  $\text{M}^{\text{I}}\text{ReF}_6$ , corresponding to  $\text{MOsF}_6$  and  $\text{MIRf}_6$ ,<sup>3</sup> has not been reported. Apart from the pentachloride,  $\text{ReCl}_5$ , the literature contains few references to compounds in which rhenium indisputably has a valency of five, and this unusual oxidation state has been little investigated.

Weise<sup>2</sup> has reported the formation of the complex oxyfluoride  $\text{K}_2\text{ReOF}_5$  by a side reaction occurring during the preparation of the quadrivalent  $\text{K}_2\text{ReF}_6$ , but he was unable to make complex fluorides of quinquevalent rhenium, e.g.,  $\text{KReF}_6$  or  $\text{K}_2\text{ReF}_7$ , by direct methods such as the action of elementary fluorine on potassium chlororhenate,  $\text{K}_2\text{ReCl}_6$ , or on mixtures of rhenium metal and potassium chloride. Parallel experiments in these laboratories with bromine trifluoride as the fluorinating agent have also been fruitless.

This suggests that the desired quinquevalent compounds are unstable and have a strong tendency to disproportionate; this is already known to be the case with the pentachloride  $\text{ReCl}_5$ , which gives  $\text{K}_2\text{ReCl}_6$  and not the expected  $\text{KReCl}_6$  when heated with potassium chloride. Clearly, therefore, methods employing strongly oxidising agents such as fluorine or bromine trifluoride, especially at high temperatures, are to be avoided, since these lead only to the hexafluoride  $\text{ReF}_6$ .

The present work describes the successful preparation of the series  $\text{M}^{\text{I}}\text{ReF}_6$  by an indirect method. This approach was suggested by an observation by Ruff and Kwasnik,<sup>4</sup> that rhenium hexafluoride,  $\text{ReF}_6$ , releases iodine from potassium iodide. Preliminary experiments with this reaction gave a product of indefinite composition even when the potassium iodide was finely powdered, and showed that it starts below  $0^\circ$ , and is not complete at  $300^\circ$ . Apparently a coating of reaction products formed on the iodide crystals protects them from further attack. The use of a solvent avoids this difficulty, and the present preparative method has depended on finding one in which both rhenium hexafluoride and potassium iodide dissolve unchanged. Only two common materials satisfy these conditions, namely elementary iodine and sulphur dioxide; since the small liquid range of the former is a decided disadvantage, the latter was chosen. Both potassium iodide and rhenium hexafluoride are soluble in liquid sulphur dioxide near its boiling point, and can be recrystallised from it unchanged. When the two solutions are brought together, iodine is liberated even at  $-60^\circ$  and heat is evolved. A white precipitate of potassium fluororhenate(v)  $\text{KReF}_6$  is formed.



If excess of rhenium hexafluoride is used the salt is easily purified as, apart from the complex itself, both reactants and products are volatile and can be removed at  $200^\circ$  in a vacuum. The substitution of other alkali iodides for that of potassium yields the corresponding quinquevalent fluororhenates, but attempts to extend the method to the preparation of the calcium and barium salts have failed, presumably because their iodides are not sufficiently soluble in liquid sulphur dioxide.

<sup>1</sup> Peacock, *J.*, 1956, 1291.

<sup>2</sup> Weise, *Z. anorg. Chem.*, 1956, 283, 377.

<sup>3</sup> Hepworth, Robinson, and Westland, *J.*, 1954, 4268.

<sup>4</sup> Ruff and Kwasnik, *Z. anorg. Chem.*, 1932, 209, 113.

All the quinquevalent fluororhenates are white crystalline powders which attack glass at about 300°; they are extraordinarily sensitive to traces of moisture and rapidly darken when exposed to moist air. Water and alkali cause vigorous hydrolysis; dark brown hydrates of rhenium oxide are formed and the solution gives the reactions for fluoride, per-rhenate, and fluororhenate(IV) ( $\text{ReF}_6^{2-}$ ) ions. Rough analysis shows that about 20% of the rhenium becomes  $\text{ReF}_6^{2-}$  ion; this behaviour contrasts sharply with that of the quinquevalent fluoro-osmates, which yield  $\text{OsF}_6^{2-}$  almost quantitatively in slightly alkaline solution. The hydrolysis of potassium fluororhenate(v) can be represented by two reactions, with the first predominating:



Rhenium pentachloride  $\text{ReCl}_5$  hydrolyses in water in an analogous way to give  $\text{ReO}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{HReO}_4$ , and  $\text{H}_2\text{ReCl}_6$ .

Crystallographically the quinquevalent fluororhenates resemble the corresponding salts of antimony, niobium, and tantalum rather than those of osmium and the other platinum metals (Table), as is shown by the sodium and potassium compounds.  $\text{KReF}_6$ , however, shows a slight tetragonal modification of the cubic (caesium chloride) structure adopted by  $\text{KNbF}_6$  and  $\text{KTaF}_6$ . The unit cell dimensions indicate that  $\text{Re}^{5+}$  is about the same size as  $\text{Sb}^{5+}$ .

*Unit-cell dimensions (lengths in Å, with  $\alpha_0$  in parentheses) of some  $\text{ABF}_6$  compounds.*

	$\text{ReF}_6^-$	$\text{NbF}_6^-$	$\text{TaF}_6^-$	$\text{SbF}_6^-$	$\text{OsF}_6^-$
Na .....	$a_0 = 8.18$	8.27*	8.27*	8.18 <sup>b</sup>	5.80 (55.2°)
K .....	$a_0 = 10.26$ ; $c_0 = 10.01$	10.29*	10.29*	10.15*	4.99 (97.2°)*
Rb .....	5.11 (96.7°)	5.14 (96.4°)*	5.14 (96.4°)*	5.11 (96.5°) <sup>d</sup>	—
Cs .....	5.28 (95.9)	5.32 (95.8)*	5.32 (95.8)*	5.32 (96.9) <sup>d</sup>	5.28 (96.1)*

Cox, J., 1956, 876. <sup>b</sup> Schrewelius, *Z. anorg. Chem.*, 1938, **233**, 241. \* Bode and Voss, *ibid.*, 1951, **264**, 144. <sup>d</sup> Schrewelius, *Arkiv Kemi*, 1942, **B**, **16**, No. 7. \* Hepworth and Jack, *J. Inorg. Nuclear Chem.*, 1956. <sup>f</sup> *Idem*, personal communication.

### EXPERIMENTAL

*Preparation of Quinquevalent Fluororhenates.*—Rhenium hexafluoride was prepared from the elements. Commercial sulphur dioxide was fractionated and the purified gas dried carefully over phosphoric oxide. The alkali iodides, which were either "AnalaR" or prepared from "AnalaR" reagents, were dried at 100° in a vacuum before use.

The reaction bulb, containing the powdered iodide, was cooled to -65° and the sulphur dioxide in sufficient excess (about 10 ml. for 0.2 g. of solid) condensed upon it. Before the salt had dissolved appreciably the bulb was cooled further with liquid oxygen and rhenium hexafluoride was allowed to sublime on top of the now solidified solvent. Dry air was then admitted and the bulb allowed to warm slowly so that the reactants dissolved in the sulphur dioxide before coming into contact with one another. When the two solutions came into contact iodine was released and a vigorous reaction set in which was controlled by judicious cooling. After visible action had ceased the mixture was boiled gently for 15 min. with constant shaking to complete the reaction. The solvent was then evaporated off completely; this removed at the same time most of the excess of rhenium hexafluoride. The remaining hexafluoride was pumped off; the iodine was removed by gradual warming to 200° in a high vacuum leaving the *quinquevalent fluororhenates* [Found: Re, 54.5; F, 33.8%; K equiv., 346.  $\text{KReF}_6$  requires Re, 54.9; F, 33.6%; K equiv., 339. Found: Re, 48.8; F, 28.7%; Rb equiv., 387.  $\text{RbReF}_6$  requires Re, 48.3; F, 29.6%; Rb equiv., 386. Found: Re, 43.1; F, 26.3%; Cs equiv., 433.  $\text{CsReF}_6$  requires Re, 42.9; F, 26.3%; Cs equiv., 433. Found: Re, 57.3; F, 35.4.  $\text{NaReF}_6$  requires Re, 57.6; F, 35.3%.]

*Analysis.*—The compounds were broken down by mixing with a large excess of moist fusion mixture and heating gradually in air to incipient redness to ensure oxidation of all the rhenium

to the septavalent state. Rhenium was determined as nitron per-rhenate and fluorine as lead chlorofluoride. Equivalent weights were based on the weights of alkali iodides used.

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