

The Reactions of Potassium Hexanitrorhodate(III) and Hexanitroiridate(III) with Potassium Hydrogen Difluoride.

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The complex fluorides K_3RhF_6 and K_2IrF_6 are formed by interaction of the corresponding trivalent complex nitrites with fused potassium hydrogen fluoride. The hydrolysis of K_3RhF_6 is described.

THE preparation of fluorine compounds of the platinum metals has, with few exceptions, required the use, directly or indirectly, of elementary fluorine. Meyer and Kienitz (*Z. anorg. Chem.*, 1939, **242**, 281), however, reported making a hydrate of rhodium trifluoride from the action of concentrated hydrofluoric acid on sodium hexanitrorhodate(III) $Na_3Rh(NO_2)_6$ and stated that potassium, rubidium, and caesium hexanitrorhodates could, under similar conditions, give the complex fluorides K_3RhF_6 , Rb_3RhF_6 , and Cs_3RhF_6 . The reaction between potassium hexanitroiridate(III) and hydrofluoric acid has not been described.

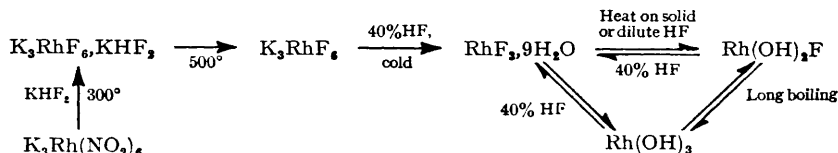
Attempts to repeat this rhodium work or to apply it to iridium have not been successful. Qualitative experiments showed that although $K_3Rh(NO_2)_6$ and $K_3Ir(NO_2)_6$ dissolve slowly in 40% aqueous hydrofluoric acid with the evolution of nitrous fumes, residues are left, even after several complete evaporations to dryness, which still contain appreciable amounts of combined nitrogen oxides. More drastic conditions are clearly required to eliminate these completely, and fusion with potassium hydrogen difluoride appeared a convenient way of attaining this end.

Potassium hexanitrorhodate(III) dissolves in potassium hydrogen difluoride, evolving nitrous fumes copiously and leaving a buff-coloured solid on cooling. According to the temperature to which the melt has been taken, two different nitrogen-free compounds are left as insoluble residues when it is leached with cold water. After being heated at about 300° the material isolated is a cubic phase of composition $K_3RhF_6 \cdot KHF_2$, but at about 500°, a temperature at which all the potassium hydrogen difluoride is converted into normal potassium fluoride, potassium hexafluororhodate(III) K_3RhF_6 is formed. This is a buff-coloured powder, and if prepared with dry materials has the composition represented by the formula. The variability first found in the analysis proved to be due to moisture in the starting materials. Thus a specimen of the hexafluororhodate, repeatedly fused with moist potassium hydrogen difluoride, lost potassium fluoride to such an extent that its composition approached K_2RhF_5 . Potassium cryolite is said to behave in a similar manner on hydrolysis (Paine and Pearson, *J.*, 1947, 1172). The compound is almost completely insoluble in cold water, and only gradually hydrolysed by hot water, but is decomposed rapidly by moist air at 300°. It is soluble in dilute hydrochloric and sulphuric acids, evidently with hydrolysis as the complex fluoride cannot be recovered from solution.

Of special interest is the reaction with hydrofluoric acid. The salt is easily soluble in 40% hydrofluoric acid, and the solution, initially red, becomes orange in a few seconds. After evaporation nearly to dryness at room temperature, red, six-sided plates of hydrated rhodium trifluoride $RhF_3 \cdot 9H_2O$ separate, which on drying at 80° form an orange-brown powder of approximate composition $Rh(OH)_2F$. The same hydroxyfluoride is obtained by either boiling or diluting the original solution in hydrofluoric acid [cf. $Al(OH)_2F$; Scott and Cowley, *J. Amer. Chem. Soc.*, 1948, **70**, 105]. $Rh(OH)_2F$ is insoluble in water, but long boiling of its suspension in water leads to the progressive loss of fluorine and eventual complete hydrolysis to the trihydroxide. With concentrated hydrofluoric acid the solution of hydrated trifluoride is re-formed.

Potassium hexanitroiridate(III) $K_3Ir(NO_2)_6$, treated with fused potassium hydrogen difluoride, yields reddish-purple potassium hexafluoroiridate(IV) K_2IrF_6 , identical in properties with the material obtained by Hepworth, Robinson, and Westland (*J.*, 1954, 4268). No evidence was obtained of any complex fluorides of trivalent iridium, and it appears that under the conditions employed Ir(III) is completely oxidised to Ir(IV).

Reduction of a solution of potassium hexafluoroiridate(IV) in hydrofluoric acid with alcohol yields a green solution containing Ir(III), but attempts to isolate a pure hydrated trifluoride have not been successful.



EXPERIMENTAL

Potassium hexanitrorrhodate, $\text{K}_3\text{Rh}(\text{NO}_2)_6$, was added in small quantities to a large excess of molten KF, HF , in which it dissolved evolving oxides of nitrogen, the colour of the melt becoming first orange and then pink as heating was continued. At about 200° the liquid became clear, and at 300° nitrogen dioxide ceased to be evolved. When cold this melt was extracted with cold water, and left a red or buff, powdery residue which was centrifuged and washed successively with cold water, alcohol, and ether, and analysed [Found: K, 37.6; Rh, 25.5; F, 36.6. Calc. for $\text{K}_3\text{RhF}_6, \text{KHF}_2$: K, 37.8; Rh, 25.0; F, 36.9%].

In another experiment the temperature of the melt was raised to about 500° and kept thereat until it ceased to give off hydrogen fluoride and became solid. Analysis showed the buff-coloured residue left on extraction of this material to be potassium hexafluororhodate(III) (Found: K, 35.1; Rh, 29.7; F, 34.1. Calc. for K_3RhF_6 : K, 35.1; Rh, 30.8; F, 34.1%).

A solution of the hexafluororhodate in 40% hydrofluoric acid, on evaporation at laboratory temperature nearly to dryness, gave crystals of hydrated rhodium trifluoride. These were hand-picked from the solution and analysed (Found: Rh, 30.1; F, 18.4. Calc. for $\text{RhF}_3 \cdot 9\text{H}_2\text{O}$: Rh, 31.9; F, 17.7%). On being heated to 80° these crystals fell to a buff-coloured powder, which analysis showed to be a hydrolytic product approaching the composition of the hydroxyfluoride [Found: Rh, 54.5; F, 12.5%; Rh:F = 1:1.24. Calc. for $\text{Rh}(\text{OH})_2\text{F}$: Rh, 66.1; F, 12.2%; Rh:F = 1:1]. This was also formed when a solution of the hexafluororhodate in hydrofluoric acid was either diluted or heated for some time (Found: Rh, 68.2; F, 9.7%). Further washing of the hydroxyfluoride with boiling water progressively leached out the fluorine; a typical sample after being washed with 100 ml. of water had F, 2.4%.

Potassium hexanitroiridate(III) $\text{K}_3\text{Ir}(\text{NO}_2)_6$, fused with KF, HF , gave potassium hexafluoroiridate(IV) (Found: Ir, 49.5. Calc. for K_2IrF_6 : Ir, 50.1%). X-Ray examination showed a material identical with the K_2IrF_6 described by Hepworth, Robinson, and Westland.

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