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Abstract

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SYNTHESIS OF COMPLEX FLUORIDES OF HEXAVALENT RHENIUM

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Complex salts of hexavalent rhenium have not hitherto been described. I. Noddack and W. Noddack (^{1}) reported the preparation of solutions of rhenium-VI oxychloric acid and its potassium salt; however, owing to the extreme instability of these compounds in aqueous medium, they were not isolated from solution. The reason for the instability of hexavalent rhenium compounds in aqueous solutions is their readily occurring hydrolysis, followed by disproportionation according to the scheme $3\mathrm{Re}^{\mathrm{VI}} \rightarrow \mathrm{Re}^{\mathrm{IV}} + 2\mathrm{Re}^{\mathrm{VII}}$. The same authors mentioned only a thiocyanate compound of composition $C_5H_5NHNCS \cdot ReO(CNS)_4$, isolated by them.

Hargreaves and Peacock (^{2}) recently reported the interaction of rhenium hexafluoride with potassium fluoride in solutions of iodine pentafluoride or liquid SO_2. The authors believe that potassium octafluororhenate, K_2ReF_8, is formed in this process. However, chemical analysis of the isolated substance is inconsistent with this formula, and the Debyeogram showed the presence of potassium fluoride in it.

In the present work it proved possible to synthesize potassium octafluororhenate by a direct reaction between liquid rhenium hexafluoride and potassium fluoride. The reaction was carried out in a Teflon test tube, into which 25 g of rhenium hexafluoride, obtained by fluorination of the metal with chlorine trifluoride according to the method described by us (^{3}), was placed. Then, with cooling, finely ground potassium fluoride (6.54 g) was added in small portions. The operations were carried out in a dry chamber cooled below zero. The reaction between the reagents taken proceeds with noticeable heating. When all the KF had been introduced into the test tube, the latter was tightly closed and heated to 20°C. After standing for 12 hours at this temperature, the reaction was complete. Excess rhenium hexafluoride was removed by distillation under vacuum, and the product obtained was again finely ground and treated once more with 2–3 g of ReF_6, after which the volatile portion was again pumped off under vacuum. The analytical results for the product before and after the repeated treatment showed constancy of composition. The weight of the product obtained (23.4 g) corresponded to that calculated from the equation

Fig. 1

Figure 1: Fig. 1

$$\mathrm{ReF_6 + 2KF = K_2ReF_8}, \tag{1}$$

based on the potassium fluoride taken. The product obtained contained small amounts of adsorbed ReF_6, had a cream color, and was vigorously decomposed by water with liberation of a black precipitate.

In the total mass of the product rather large crimson-colored crystals were encountered. These crystals were practically insoluble in water and were destroyed by it very slowly, giving soluble products. Owing to these properties with respect to water, the crimson crystals could be isolated in pure form by treating with ice water the product obtained by the reaction of rhenium hexafluoride with KF according to the method described above. However, to obtain the crimson salt it is necessary to modify the procedure, eliminating the excess of rhenium hexafluoride and taking equivalent amounts of the starting substances.

In this case a raspberry-colored product is obtained, which consists almost entirely of potassium octafluororhenate. In order to purify this product from an admixture of potassium fluoride, it was washed with ice water and methyl alcohol and dried in vacuum. Chemical analysis confirms that the composition of the raspberry-colored salt corresponds to the formula K_2ReF_8.

Fig. 1

Figure 1 shows a sketch of a crystal of potassium octafluororhenate. In the plane of the drawing the crystals are biaxial, possess straight extinction and, consequently, belong to the rhombic system. The elongation of the crystals is positive.

In air, potassium octafluororhenate is fairly stable and begins to decompose only after several hours; its bright raspberry color fades and changes to blue, after which blackening rapidly occurs. In water potassium octafluororhenate is practically insoluble, but slowly undergoes hydrolysis, forming a blue product soluble in water with formation of a blue solution. Hot water dissolves the octafluororhenate with formation of a green solution, which soon assumes a brown color as a result of hydrolysis. The salt is well preserved in polyethylene ampoules. On contact with glass it rapidly decomposes, corroding the surface of the glass.

Potassium octafluororhenate dissolves in hydrogen fluoride with decomposition, liberating rhenium hexafluoride according to the scheme:

$$\mathrm{K_2ReF_8} + n\mathrm{HF} \rightarrow \mathrm{ReF_6} + 2\mathrm{KF} \cdot n\mathrm{HF}. \tag{2}$$

Rhenium hexafluoride itself is sparingly soluble in hydrogen fluoride, giving a colorless solution. When such a solution is evaporated in a stream of dry nitrogen, rhenium hexafluoride volatilizes together with the hydrogen fluoride, while a saturated solution of potassium fluoride in hydrogen fluoride remains in the residue, from which crystals of acid fluorides precipitate. The collected condensate, after removal of hydrogen fluoride from it under vacuum at −70°, was again used to obtain potassium octafluororhenate.

As indicated above, potassium octafluororhenate slowly reacts with water, forming a blue product. However, in view of the rapid decomposition of this product, it was not possible to isolate it from an aqueous solution. A compound having the same blue color can be isolated from a hydrogen fluoride solution. It was observed that a solution of K_2ReF_8 in HF, on standing in air, acquired a blue color, while the solid phase, consisting in accordance with equation (2) of rhenium hexafluoride, passed entirely into solution. When K_2ReF_8 was dissolved in hydrogen fluoride containing a certain amount of water (0.02%), a transparent blue solution was obtained, from which, after cooling to −70°, a crystalline blue substance separated. The solution was then decanted, and the residues of hydrogen fluoride were removed from the solid residue in vacuum. The blue product had a homogeneous crystalline structure; its composition corresponded to the formula $K_2ReOF_6 \cdot 2HF$ and represented potassium oxyhexafluororhenate with two molecules of HF. In water at 0° this salt is appreciably soluble, forming a blue solution which after 10 min turns green and then rapidly acquires a brown color. Potassium oxyhexafluororhenate dissolves readily in hydrogen fluoride, and upon hydration of this solution the blue color of the solution changes to green and then to brown. From the green solutions, on cooling, large green crystals precipitated. Although no analysis of them was carried out, it may nevertheless be assumed that this salt is a product of further hydrolysis of potassium oxyhexafluororhenate, for example to $K_2ReO_2F_4$.

The analytical method, as described in the analysis of rhenium hexafluoride (2), was based on hydrolysis of the sample with a definite amount of alkali with simultaneous

by simultaneous oxidation of the sample with hydrogen peroxide. The excess alkali was titrated. The amount of alkali required for neutralization was calculated from the equations:

$$2\,K_2ReF_8 + 14\,NaOH + H_2O_2 = 2\,KF + 2\,KReO_4 + 14\,NaF + 8\,H_2O; \qquad (3)$$

$$2\,K_2ReOF_6 \cdot 2HF + 14\,NaOH + H_2O_2 = 2\,KF + 2\,KReO_4 + 14\,NaF + 10\,H_2O. \qquad (4)$$

Table 1 gives the results of calculations of the required amount of alkali in gram-equivalents per 1 g of salt and the quantities obtained. Rhenium was then determined in the solution as nitron perrhenate, and fluorine by titration with an $AlCl_3$ solution. Potassium was determined as the sulfate in the solution after removal of rhenium as the sulfide.

Table 1

Chemical-analysis data for complex rhenium fluorides

Compound	K content, %, found	K content, %, calculated	Re content, %, found	Re content, %, calculated	g-equiv. alkali, found	g-equiv. alkali, calculated	F content, %, found	F content, %, calculated
K_2ReF_8 potassium octafluororhenate (raspberry-colored salt)	18.6 ±0.2	18.8	44.6 ±0.2	44.7	0.165 ±0.002	0.168	36.2 ±0.1	
$K_2ReOF_6 \cdot 2HF$ potassium oxyhexafluororhenate (blue salt)	17.6 ±0.2	17.9	42.7 ±0.2	42.9	0.160 ±0.001	0.161	34.7 ±0.2	

Potassium octafluororhenate is an analogue of complex compounds based on the hexafluorides of molybdenum, tungsten, and uranium, for which Martin and Albers (4) and Cox, D. Sharp, and A. Sharp (5) synthesized potassium salts of compositions K_2MeF_8, whereas with heavier cations salts of composition $MMoF_7$ and MWF_7 (6) are obtained, where M is rubidium or cesium. As for potassium oxyhexachlororhenate, there is at present a report (6) on the preparation of complex oxyfluoro salts of molybdenum and tungsten derived from the fluoroxy acids $MeOF_4$ and having the compositions $CsMoOF_5$ and $CsWOF_5$.

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REFERENCES

1. I. Noddak, W. Noddak, *Zs. anorg. u. allgem. Chem.*, **215**, 129 (1933).
2. G. B. Hargreaves, R. D. Peacock, *J. Chem. Soc.*, 1958, 4390.
3. N. S. Nikolaev, E. G. Ippolitov, DAN, **134**, No. 2 (1960).
4. H. Martin, A. Albers, *Naturwiss.*, **133**, 370 (1946).
5. B. Cox, D. W. Sharp, A. G. Sharp, *J. Chem. Soc.*, 1956, 1242.
6. G. B. Hargreaves, R. D. Peacock, *J. Chem. Soc.*, 1958, 2171.

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