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Abstract

Full Text

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On the Interaction of Rhenium Hexafluoride with Metal Fluorides

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The first representative of the complex fluorides of hexavalent rhenium—potassium octafluororhenate—was obtained by us earlier ([1]) by the reaction of ReF_6 with KF. The present communication concerns the interaction of rhenium hexafluoride with alkali-metal fluorides in a melt of ReF_6 and in a solution of ClF_3. The latter method was analogous to the method developed by N. S. Nikolaev and V. F. Sukhoverkhov for obtaining complex fluorides of hexavalent Mo, W, and U ([2]).

Metal fluorides were prepared from carbonates and chemically pure hydrofluoric acid. Rhenium hexafluoride was obtained by two methods. The first of these is based on combustion of rhenium in a stream of chlorine trifluoride diluted with nitrogen, and has already been described by us ([3]). Preparations synthesized by this method are distinguished by high purity; they were used as standards. A faster method for obtaining ReF_6 is based on the reaction of fluorine with metallic rhenium at 150° in a nickel reactor. In a typical case, 20 g of rhenium was burned over 6 hr. The product was collected in a Teflon receiver. For purification it was distilled in a stream of hydrogen. Rhenium hexafluoride obtained by this method was completely identical with that synthesized by the first method.

Fig. 1. Thermal decomposition of $KReF_7$.

For carrying out the reaction of ReF_6 with metal fluorides, a Teflon autoclave was used, capable of withstanding the vapor pressure of rhenium hexafluoride at 200°. All operations for conducting such experiments were carried out in a dry box cooled with liquid nitrogen. Rhenium hexafluoride was loaded into the autoclave by weight; then an alkali-metal fluoride, freshly calcined at a temperature close to its melting point, was added to it from a platinum test tube. The reagents were mixed; then the autoclave was tightly closed, removed from the box, and heated at the specified temperature.

Fig. 2. Thermal decomposition of K_2ReF_8

Figure 2: Fig. 2. Thermal decomposition of K_2ReF_8

On the basis of extensive experimental material it was established that all alkali fluorides, with the exception of lithium fluoride, react, depending on the conditions, in two stages according to the schemes:

$$ReF_6 + 2MeF = Me_2ReF_8; \tag{1}$$

$$Me_2ReF_8 + ReF_6 \rightleftarrows 2MeReF_7. \tag{2}$$

Equation (1) describes the reaction of ReF_6 and alkali-metal fluorides taken in a molar ratio of $1 : 2$ at temperatures up to 200°. In this case, pink octafluororhenates of composition Me_2ReF_8 are formed, where Me—Na, K, Rb, and Cs. The octafluororhenates, with the exception of sodium octafluororhenate, add one more molecule of rhenium hexafluoride at lower temperatures according to scheme (2). In this case, yellow heptafluororhenates of composition $MeReF_7$ are formed, where Me—K, Rb, and Cs. These compounds differ sharply from the octafluororhenates in color, crystal form, and chemical properties.

The thermal stability of heptafluororhenates decreases in the series Cs > Rb > K > Na. Sodium heptafluororhenate cannot be obtained at all, and potassium heptafluororhenate begins to dissociate according to equation (2) already at 50°. After prolonged standing in vacuum it is converted into potassium octafluororhenate. Figures 1 and 2 show thermogravimetric curves obtained on heating $KReF_7$ and K_2ReF_8 in a stream of dry nitrogen. From Fig. 1 it is evident that rapid decomposition of $KReF_7$ occurs at 200-300°. In this process rhenium hexafluoride is evolved, which can be trapped. The weight of the residue after thermal decomposition is equal to 59% of the weight of the $KReF_7$ taken, which corresponds to the weight of potassium octafluororhenate calculated from equation (2).

Fig. 2. Thermal decomposition of K_2ReF_8

The thermal stability of the latter is remarkable. From Fig. 2 it is evident that even at 500° no decomposition is observed. Only at about 700° does a slight loss of weight occur and a heterogeneous yellow product form. The heptafluororhenates of Rb and Cs are more stable than potassium heptafluororhenate, but nevertheless, on heating them with the corresponding fluorides at 200°, they pass completely into octafluororhenates according to the scheme

$$MeReF_7 + MeF = Me_2ReF_8. \tag{3}$$

All the synthesized compounds and their properties are given in Table 1.

Table 1

Properties of complex fluorides of ReVI

Compound	Color	Thermal stability	Stable in open air	Relation to water	Solubility in organic solvents	Magnetic moment, μB	Density
Na_2ReF_8	pink	stable	less stable than K_2ReF_8	readily soluble	decomposes in methyl alcohol	1.69	
K_2ReF_8	pink	stable	stable for 10 h	sparingly soluble	insoluble in methyl alcohol	1.6	4.35 g/cm^3
Rb_2ReF_8	pink	stable	stable almost like K_2ReF_8	insoluble	insoluble in methyl alcohol	1.65	4.5 g/cm^3
Cs_2ReF_8	pink	stable	rapidly decomposes	readily decomposes	insoluble in methyl alcohol	1.71	
$KReF_7$	yellow	dissociates at 50°	rapidly decomposes	readily soluble*	decomposes in methyl alcohol	0.6	
$RbReF_7$	yellow	dissociates at 100°	decomposes	readily soluble*	soluble in methyl alcohol	0.7	
$CsReF_7$	yellow	dissociates at 200°	decomposes	soluble*	soluble in methyl alcohol	0.7	

* With careful dissolution in ice water. Otherwise it decomposes.

Note. decomposes–decomposes; stable–stable; soluble–soluble; readily soluble –readily soluble; insoluble–insoluble; soluble in methanol–soluble in methyl alcohol; dissociates–dissociates according to equation (2).

1. Potassium octafluororhenate was synthesized by two methods. In the first of them, KF was heated in an autoclave at 200° with rhenium hexafluoride

Fig. 3. X-ray spectra of octafluororhenates

Figure 3: Fig. 3. X-ray spectra of octafluororhenates

in a molar ratio of 2 : 1 for 6 h. The resulting product was washed free of ReF_6 with chlorine trifluoride. Residual ClF_3 was removed by gentle heating; then the resulting product was washed with water to remove heptafluororhenate impurity and with absolute alcohol; traces of the latter were removed in vacuum. Yield 95%. By the second method, a coarse-crystalline ···

Fig. 3. X-ray spectra of octafluororhenates

chemically pure potassium octafluororhenate. The method is based on recrystallization of the latter from ReF_6. For this purpose, a mixture of KF and ReF_6 in a molar ratio of 0.3 : 1 was taken and heated at 200° for 4 hours; then the autoclave was opened slightly and the excess ReF_6 was released. The remaining product was washed with chlorine trifluoride.

2. Sodium and rubidium octafluororhenates were obtained in the same way as potassium octafluororhenate by the first method. However, the sodium salt was not washed with water.

3. Cesium octafluororhenate was obtained by heating ReF_6 with an excess of cesium fluoride. A mixture was taken in a molar ratio of 1 : 2.2 and heated in an autoclave at 200° for 48 hours. The product was washed free of CsF with chlorine trifluoride, in which it is readily soluble (?).

4. Potassium heptafluororhenate was obtained by mixing ReF_6 and KF, taken in a molar ratio of 1 : 0.5. The reaction mixture was kept at 0° for 36 hours. The product was washed with chlorine trifluoride.

5. Rubidium and cesium heptafluororhenates were obtained in the same way as potassium heptafluororhenate, but a smaller excess of ReF_6 was taken, and the reaction was carried out at room temperature for 6 hours.

6. $CsReF_8$ and $CsReF_7$ were also obtained by mixing solutions of ReF_6 and CsF in ClF_3, taken in the corresponding molar ratio.

Table 2

Results of analysis of the synthesized compounds

Compound	Re, % calculated	Re, % found	Me, % calculated	Me, % found	F, % calculated	F, % found
Na_2ReF_8	48.5	48.6	12.0	11.6	29.6	29.7
K_2ReF_8	44.7	45.2	18.8	18.3	36.5	36.7
Rb_2ReF_8	36.6	37.0	33.6	33.0	29.8	29.6

Compound	Re, % calculated	Re, % found	Me, % calculated	Me, % found	F, % calculated	F, % found
Cs_2ReF_8	30.8	30.6	44.0	43.9	25.2	24.9
$KReF_7$	52.0	51.8	10.9	11.0	37.1	37.4
$RbReF_7$	46.0	45.8	21.1	20.9	32.9	33.0
$CsReF_7$	41.2	40.9	29.4	29.2	29.4	29.8

The synthesized salts were subjected to complete chemical analysis. The results of the analysis are given in Table 2. The method for determining fluorine and rhenium has been described previously ([1]). The alkali elements were determined by evaporating to dryness the solution obtained after oxidation of the sample in a platinum crucible. The residue—a mixture of fluoride and perrhenate—was weighed.

Microscopic observations of the salts obtained confirmed that they consist of a single crystalline phase.

The sodium, potassium, and rubidium octafluoroperrhenates proved sufficiently stable that their X-ray spectra could be obtained in an ionization chamber.* Figure 3 b, c, and d gives the X-ray spectra of sodium, potassium, and rubidium octafluoroperrhenates, obtained at a rate of 0.5 degree per minute, with iron radiation and a manganese filter. The spectra of the potassium and rubidium salts are reproduced exactly upon repeated rotation of the same sample. The spectrum of the sodium salt is not completely reproduced, owing to appreciable decomposition during the measurement.

The density of potassium octafluoroperrhenate was measured and was found to be 4.35 g/cm^3. The magnetic moment of all the octafluoroperrhenates is 1.7-1.6 μB, which is in full agreement with the hexavalent state of rhenium.** The heptafluoroperrhenates are also paramagnetic, but their magnetic moment is less than the calculated value.

All octafluoroperrhenates, except the sodium salt, are almost insoluble in water. On standing with water for several minutes, the solution above them acquires a blue color. Sodium octafluoroperrhenate in water immediately gives a blue solution. After 10 min this solution acquires a brown coloration as a result of the disproportionation reaction characteristic of compounds of hexavalent rhenium:

$$3Me_2ReF_8 + 12H_2O = 2MeReO_4 + ReO_2 \cdot 2H_2O + 2OHF + 4MeF. \quad (4)$$

This process is sharply accelerated when the solution is heated. In contrast to the octafluoroperrhenates, all the heptafluoroperrhenates are readily soluble in cold water, with formation of blue solutions analogous to those obtained from octafluoroperrhenates.

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3. N. S. Nikolaev, E. G. Ippolitov, DAN, 134, No. 5, 358 (1960).

* Measurements were made on an apparatus in the laboratory of V. G. Kuznetsov.
** Measurements were made by V. I. Belova in the laboratory of Ya. K. Syrkin.

Note: Figure translations are in progress. See original paper for figures.