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Abstract

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Synthesis and Study of Rhenium(IV) Aminohalides

Preparation and Properties of Rhenium Dipyridinetetrabromide

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Tetravalent rhenium, like Pt^IV, forms stable complex compounds with bromine of the type $M_2^I[ReX_6]$ and $M_2^I[ReOHX_5]$ ([1,2]). These compounds are distinguished by high thermal stability ([3]). In comparison with complex chlorides, the ions $[ReBr_6]^{2-}$ are characterized by a greater tendency toward hydrolysis, as a result of which only solutions in concentrated HBr are stable ([2]). In aqueous, weakly acidic, neutral, and still more alkaline solutions, bromorhenates are completely unstable.

This explains the absence of literature data on the existence of aminobromorhenates ([4]), for example compounds similar to the previously obtained $[RePy_2Cl_4]$ ([5]), which has the properties of a nonelectrolyte and is analogous to the cis- and trans-isomers of Pt, in particular the salts of Klee and Gerhard. As was already indicated ([6]), attempts to obtain complex aminohalides of Re^IV did not lead to positive results, and until recently the only known representative of them was rhenium dipyridinetetrachloride. In a work published in 1959, the preparation of rhenium dipyridinetetraiodide ([7]) was reported, and the suggestion was made that rhenium dipyridinetetrabromide could be obtained by the same method.

In this connection, it seemed of interest to us to present in this communication some information on the results of experiments on the synthesis of $[RePy_2Br_4]$ by the same methods by which $[RePy_2Cl_4]$ was obtained, i.e., by thermal decomposition of pyridinium hexahalorhenate according to the scheme:

$$(PyH)_2[ReX_6] \rightarrow 2HX + [RePy_2X_4], \quad (1)$$

as well as by heating it with anhydrous pyridine at 200° ([5,8]).

First of all, we synthesized the previously unknown pyridinium hexabromorhenate $(PyH)_2[ReBr_6]$, which served as the starting material in the synthesis of $[RePy_2Br_4]$, and studied the nature of its thermal decomposition. The heating curve, recorded in argon, had four endothermic effects (Fig. 1), which indicated a stepwise decomposition of the compound with the formation of intermediate products. Interpretation of the first effect (320°) showed that, analogously to

$(PyH)_2[ReCl_6]$, decomposition of pyridinium hexabromorhenate proceeds with the elimination of two molecules of HBr and the incorporation of pyridine into the inner sphere of the complex.

Study of the solubility and electrical conductivity of the $[RePy_2Br_4]$ thereby formed confirmed that the compound is a nonelectrolyte, stable in aqueous solutions up to 100°. Rhenium dipyridinetetrabromide, like $[RePy_2Cl_4]$, is insoluble in water and acids, but in contrast to it, when heated in a weakly alkaline solution with H_2O_2, it is gradually hydrolyzed. On boiling with an aqueous 25% ammonia solution, hydrolysis of the compound proceeded instantaneously, whereas $[RePy_2Cl_4]$ is relatively stable under these conditions.

The data obtained permit one to state quite definitely that the complex bromides of tetravalent rhenium are less stable in solutions than the complex chlorides. If the steric factor is taken into account (the bromine ion has a somewhat larger effective radius, 1.95 Å, than the chlorine ion, 1.81 Å), then the decrease in stability on passing to the bromides is quite natural. In acid solutions $[RePy_2Br_4]$ is stable, and heating in them was not accompanied by hydrolysis. With concentrated HBr at

At 320° the compound reacts according to the reaction:

$$[RePy_2Br_4] + 2HBr \xrightarrow{320^\circ} (PyH)_2[ReBr_6] \qquad (2)$$

The action of molecular hydrogen under pressure on $[RePy_2Br_4]$ in HBr solution led to the formation of a divalent rhenium compound of composition $(PyH)HReBr_4$. The compound was obtained in the form of rather large crystals, similar to $(PyH)HReCl_4$. As already indicated, $[RePy_2Cl_4]$ can be obtained by two methods: by thermal decomposition of $(PyH)_2[ReCl_6]$, and also by heating it with anhydrous pyridine in sealed ampoules at 200°, the advantage of the second method being the preparation of $[RePy_2Cl_4]$ in crystalline form. It proved that by this method one can also obtain crystalline $[RePy_2Br_4]$ with crystal sizes up to 1 mm. The identity of the products obtained by the two different methods was confirmed by comparing their properties and composition.

Experimental Part

Preparation of $(PyH)_2[ReBr_6]$**.** Pyridinium hexabromorhenate was obtained by the action of pyridine on a solution of $K_2[ReBr_6]$ in hydrobromic acid. $K_2[ReBr_6]$ was obtained by the previously described method ([1]). Taking into account the instability of solutions of potassium hexabromorhenate in dilute HBr, its dissolution was carried out in concentrated acid. To a solution of $K_2[ReBr_6]$ in HBr heated to boiling, pyridine was added in small portions. The orange crystalline precipitate separating on cooling of the solution was recrystallized from concentrated HBr. Depending on the crystallization conditions, $(PyH)_2[ReBr_6]$ separated in the form of lustrous plates or in the form of rectangular prisms,

Fig. 1. Thermogram of $(PyH)_2[ReBr_6]$

Figure 1: Fig. 1. Thermogram of $(PyH)_2[ReBr_6]$

soluble in acids, alcohols, and acetone. Hydrolysis of aqueous solutions occurred already at room temperature.

Fig. 1. Thermogram of $(PyH)_2[ReBr_6]$

Analysis of the substance was carried out by the method of fusion with soda, previously used for the analysis of complex chlorides.

Found, %:	Re 22.62,	Br 58.29;	N 2.97
$(PyH)_2[ReBr_6]$. Calculated, %:	Re 22.54;	Br 58.05;	N 3.39

Preparation of $[RePy_2Br_4]$. Figure 1 presents the heating curve of $(PyH)_2[ReBr_6]$, which has four endothermic effects. Deciphering the first effect (320°), which, as we assumed, corresponds to the formation of $[RePy_2Br_4]$, was carried out in the apparatus described for the preparation of rhenium dipyridinetetrachloride ([5]). The melt obtained after heating for 30 min at 310-320° was first treated with HBr to dissolve the unreacted starting substance, then boiled with water, dilute HNO_3, and washed on the filter with hot water, alcohol, and ether. A bright-red fine-crystalline powder was obtained, stable in aqueous solutions, insoluble in acids, and hydrolyzing when heated in 25% aqueous ammonia. The electrical conductivity at $V = 1000$ l is $9.3 \cdot 10^{-6}$ Ω^{-1}. It changed almost not at all with time.

On the heating curve of the substance (Fig. 2) there are three endothermic effects at 380, 400, and 410°. The compound is paramagnetic; the effective magnetic moment is 3.48 Bohr magnetons. The results of analysis of the substance are as follows:

Found, %:	Re 28.40,	Br 47.78;	N 4.00
$[RePy_2Br_4]$. Calculated, %:	Re 28.04;	Br 48.13;	N 4.21

The ratio Re : Br : N = 1 : 4.0 : 2.

In the form of fairly large crystals, $[RePy_2Br_4]$ was obtained by heating $(PyH)_2[ReBr_6]$ with anhydrous pyridine. Since even slightly moistened pyridine caused hydrolysis of the pyridonium hexabromorhenate, the reacting substances were placed in an ampoule, which was sealed after preliminary evacuation of the air. The ampoule was placed in an autoclave, which was heated in a thermostat for two hours at 200°. After 10-12 h, the cooled autoclave was opened, the ampoule was opened, and the solid phase, after separation from the mother liquor on a filter, was boiled with water acidified with HNO_3, and washed on the filter with hot water, alcohol, and ether. Analysis and the

Fig. 2. Thermogram of $[RePy_2Br_4]$

Figure 2: Fig. 2. Thermogram of $[RePy_2Br_4]$

properties of the product obtained by this method confirmed its identity with $[RePy_2Br_4]$ obtained by thermal decomposition of $(PyH)_2[ReBr_6]$.

Fig. 2. Thermogram of $[RePy_2Br_4]$

Found, %: Re 28.24; Br 48.88; 48.20; N 4.5

Interaction with HBr. This reaction, like the preceding one, was carried out in sealed ampoules. At 300–310°, addition of two molecules of HBr to $[RePy_2Br_4]$ occurs, with formation of $(PyH)_2[ReBr_6]$.

Found, %: Re 21.85; Br 58.16
$(PyH)_2[ReBr_6]$. Calculated, %: Re 22.54; Br 58.05

Reduction of $[RePy_2Br_4]$ by molecular hydrogen was carried out in an autoclave at 310° and a hydrogen pressure of 40 atm. The dark-brown crystals obtained of the compound $(PyH)HReBr_4$ did not dissolve in conc. HBr and underwent hydrolysis in aqueous solution upon heating.

Found, %: Re 31.64; Br 54.90; N 2.26
$(PyH)HReBr_4$. Calculated, %: Re 31.72; Br 55.45; N 2.38

Thus, pyridonium hexabromorhenate of composition $(PyH)_2[ReBr_6]$ has been synthesized. Rhenium dipyridinetetrabromide, formed upon thermal decomposition of $(PyH)_2[ReBr_6]$, has been isolated, and its properties have been studied. A method has been developed for obtaining $[RePy_2Br_4]$ in crystalline form, consisting in heating $(PyH)_2[ReBr_6]$ with anhydrous pyridine at 200°. It has been shown that, as a result of the interaction of $[RePy_2Br_4]$ with conc. HBr at 310°, addition of 2 moles of HBr occurs, with formation of pyridonium hexachlororhenate. Reduction of $[RePy_2Br_4]$ by molecular hydrogen under pressure at 300° in a solution of conc. HBr leads to formation of a compound of divalent rhenium of composition $(PyH)HReBr_4$.

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REFERENCES CITED

1. F. Krauss, H. Steinfeld, Ber., **64**, 2552 (1931).

2. C. Rulfs, R. Meyer, J. Am. Chem. Soc., **77**, 4505 (1955).

3. Miao Tsin-shen, Dissertation, 1960.

4. P. Paskal, *Nouveau traité de chimie minérale*, 1960, p. 16.

5. V. G. Tronev, G. K. Babeshkina, ZhNKh, **3**, issue 2, 2458 (1958).

6. V. V. Lebedinskii, B. N. Ivanov-Emin, ZhOKh, **13**, 256 (1943).

7. R. Colton, G. Wilkinson, Chem. Ind., No. 42, 1314 (1959).

8. G. K. Babeshkina, V. G. Tronev, ZhNKh, **7**, issue 1 (1962).

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