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On the Synthesis and Thermal Stability of Dihydrates of Zirconium and Hafnium Oxynitrates

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Zirconium and hafnium nitrates are acquiring ever greater importance in the technology of these elements, especially in connection with the development of extraction methods of separation. However, the literature contains very insufficient and contradictory data on the composition and properties of zirconium nitrates; hafnium nitrates have not been described at all.

Zirconium oxynitrates are usually obtained by evaporating nitric-acid solutions ($^{1-6}$). Depending on the evaporation temperature, compounds of various composition may form ($^{3-5,7,8}$): $3ZrO_2 \cdot 2N_2O_5$, $ZrO_2 \cdot N_2O_5$, $ZrO(NO_3)_2 \cdot 2H_2O$, $ZrO(NO_3)_2 \cdot 3\frac{1}{2}H_2O$, $ZrO(OH)NO_3$, $ZrO(OH)NO_3 \cdot 2H_2O$. According to many authors (^{9}), these oxynitrates are products of definite stages of hydrolysis of normal zirconium nitrate. Depending on the experimental conditions—the concentrations of nitric acid and zirconium and the evaporation temperature—zirconium and hafnium oxynitrates of various composition can be obtained. Zirconyl nitrate dihydrate, $ZrO(NO_3)_2 \cdot 2H_2O$, a white crystalline substance readily soluble in water, is formed when a nitric-acid solution of zirconium hydroxide is kept over concentrated H_2SO_4 (^{6}), or during its evaporation at 65° (^{5}). Raising the temperature to 100° leads to the formation of a glassy mass whose composition corresponds to the formula $ZrO(OH)NO_3$. In the course of thermal decomposition of $ZrO(NO_3)_2 \cdot 2H_2O$, oxynitrates of various composition are also observed (^{8}): $3ZrO(NO_3)_2 \cdot ZrO_2 \cdot 7H_2O$ (110°), $ZrO(NO_3)_2 \cdot 2ZrO_2 \cdot 4H_2O$ (150°), $ZrO(NO_3)_2 \cdot 7ZrO_2 \cdot 5H_2O$ (215°), $ZrO(NO_3)_2 \cdot 10ZrO_2 \cdot 4H_2O$ (250°), and only above 250° is ZrO_2 formed. Zirconium oxynitrates in which the ratio $Zr : HNO_3$ is less than $1 : 2$ dissolve poorly in water, and their aqueous solutions are strongly opalescent. It should be noted that zirconium nitrate dihydrate is obtained most readily. However, most methods for obtaining it are difficult to reproduce; usually the composition of the preparation corresponds approximately to the formula $ZrO(NO_3)_2 \cdot 2H_2O$, but it sometimes contains, in considerable amounts, other basic nitrates that are poorly soluble in water. Therefore, it is of interest to seek reproducible methods for the synthesis of individual zirconium and hafnium nitrates and to study their properties. The present communication gives the results of research in the field of the synthesis of dihydrates of zirconium and hafnium oxynitrates and data on their thermal stability.

Fig. 1. Thermograms of $ZrO(NO_3)_2 \cdot 2H_2O$ (a) and $HfO(NO_3)_2 \cdot 2H_2O$ (b). Average heating rate 8-10°/min

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In the course of slow evaporation of solutions of freshly precipitated hydroxides in concentrated HNO_3 at various temperatures not exceeding 100°, and with varying amounts of HNO_3, it was not possible to obtain an individual compound. This is probably explained by the fact that freshly precipitated hydroxides contain a very large and variable amount of water, which affects the degree of hydrolysis of the nitrate. Therefore mixtures of various basic nitrates of zirconium or hafnium are obtained. Zirconium and hafnium hydroxides dried in air to constant weight also proved unsuitable for synthesis, since upon drying their solubility in nitric acid of any concentration decreases sharply.

To avoid the difficulties that arose, zirconium (hafnium) octahydrate oxychloride was used for the synthesis; it contains the anion of a volatile acid and a strictly definite amount of water of crystallization. The starting zirconium and hafnium compounds were spectrally pure and contained only 0.03% Hf and 2% Zr, respectively. A weighed portion of the salt was treated with various amounts of 100% HNO_3; the weight ratio $MeO_2 : HNO_3$ was varied from 1 : 3 to 1 : 6. Through nitric-acid solutions, air was blown until the yellow coloration disappeared; then they were evaporated to dryness on a water bath at 60° with constant stirring. All preparations obtained in this way dissolved well in water and, according to chemical analysis, had a constant composition. Upon repeated repetition of the experiments, the results were completely reproducible. The optimal ratio $MeO_2 : HNO_3$ may be considered 1 : 4.5. In this case the chlorine content in the final product does not exceed 0.006%.

Fig. 1. Thermograms of $ZrO(NO_3)_2 \cdot 2H_2O$ (a) and $HfO(NO_3)_2 \cdot 2H_2O$ (b). Average heating rate 8-10°/min

In the compounds obtained, the contents of ZrO_2 and HfO_2 were determined gravimetrically, and N_2O_5 by Devarda' s method. The amount of water was calculated from the loss in weight obtained after igniting the substance at 900° to constant weight. The results of analyses, which are averages of 3-4 experiments, are given below:

	ZrO_2, %	HfO_2, %	N_2O_5, %	H_2O, %	$MeO_2 : N_2O_5 : H_2O$
Aqueous zirconium oxynitrate	46.24	–	39.96	13.80	1 : 0.99 : 2.02
Aqueous hafnium oxynitrate	–	58.98	30.37	10.65	1 : 1.02 : 2.10

In accordance with the analytical data, the synthesized compounds should be assigned the formulas: $ZrO(NO_3)_2 \cdot 2H_2O$ and $HfO(NO_3)_2 \cdot 2H_2O$.

The dihydrates of zirconium and hafnium oxynitrates are white crystalline substances. According to optical analysis, their crystals are anisotropic. However, the values of the refractive indices are close to one another; therefore we were able to determine only their mean values. Measurements were carried out by the immersion method at 22°. The obtained values n_{av} differ only slightly and are equal to 1.592 ± 0.001 for $ZrO(NO_3)_2 \cdot 2H_2O$ and 1.558 ± 0.001 for $HfO(NO_3)_2 \cdot 2H_2O$. The difference in the density values is also small: 2.267 and 3.144, respectively, for $ZrO(NO_3)_2 \cdot 2H_2O$ and $HfO(NO_3)_2 \cdot 2H_2O$ (the density determinations were carried out pycnometrically at $20 \pm 0.1^{\circ}$).

The transformations of zirconium and hafnium oxynitrates occurring upon heating in air were studied by several methods.

Experiments to determine the composition of the residues obtained by igniting the compounds to constant weight were carried out as follows. A weighed portion of the salts (0.1-0.5 g) was placed in a drying oven (40-200°) or in a muffle furnace (250–500°), heated to the specified temperature. The dev–

···in the temperature regime were $±$2° and $±$10°, respectively. The residues were weighed and analyzed for the content of MeO_2 and N_2O_5. The results of the study in the range 40–500° are presented in Tables 1 and 2.

Table 1

Results of heating $ZrO(NO_3)_2 \cdot 2H_2O$ and $HfO(NO_3)_2 \cdot 2H_2O$ in air to constant weight

Temperature, °C	Weight loss, %	Ratio $ZrO_2 : N_2O_5 : H_2O$	Residue	Weight loss, %	Ratio $HfO_2 : N_2O_5 : H_2O$	Residue
40	1.24	1:0.99:1.83	Crystalline	0.64	1:0.99:2.00	Crystalline

Temperature, °C	Weight loss, %	Ratio $ZrO_2 : N_2O_5 : H_2O$	Residue	Weight loss, %	Ratio $HfO_2 : N_2O_5 : H_2O$	Residue
60	1.38	1:0.95:2.20	Crystalline	1.31	1:0.97:1.62	Crystalline
80	1.66	1:0.93:2.30	Crystalline	2.00	1:0.97:1.65	Crystalline
100	2.46	1:0.92:2.30	Crystalline	4.99	1:0.06:1.00	Crystalline
120	4.39	1:0.89:2.37	Crystalline	5.31	1:1.05:1.00	Crystalline
140	36.88	1:0.30:0.90	X-ray amorphous	23.76	1:0.45:1.3	Crystalline
160	43.33	1:0.19:0.55	X-ray amorphous	31.40	1:0.28:0.48	X-ray amorphous
180	45.15	1:0.18:0.26	X-ray amorphous	33.65	1:0.18:0.56	X-ray amorphous
200	48.17	1:0.15:0.17	X-ray amorphous	35.08	1:0.14:0.48	X-ray amorphous
250	52.58	1:0.02:0.20	X-ray amorphous	39.20	1:0.05:0.21	X-ray amorphous
300	53.16	1:0.01:0.08	X-ray amorphous	39.50	1:0.01:0.40	X-ray amorphous
400	53.51*	–	Monoclinic ZrO_2	40.20*	–	Monoclinic HfO_2
500	54.37	–	Monoclinic ZrO_2	40.70	–	Monoclinic HfO_2

* In residues obtained after calcination of $ZrO(NO_3)_2 \cdot 2H_2O$ and $HfO(NO_3)_2 \cdot 2H_2O$ at 400°, traces of N_2O_5 and a small amount of H_2O (0.4–1.0 wt. %) are present.

Table 2

Results of analysis of residues of $ZrO(NO_3)_2 \cdot 2H_2O$ and $HfO(NO_3)_2 \cdot 2H_2O$, obtained in the process of heating to a specified temperature at a rate of 8-10°/min

Compound	Temperature, °C	ZrO_2, wt. %	HfO_2, wt. %	N_2O_5, wt. %	H_2O, wt. %	Ratio $MeO_2 : N_2O_5 : H_2O$
$ZrO(NO_3)_2 \cdot 2H_2O$	100	46.23	–	39.07	14.70	1:0.96:2.17
$ZrO(NO_3)_2 \cdot 2H_2O$	180	70.46	–	25.04	4.50	1:0.40:0.44
$ZrO(NO_3)_2 \cdot 2H_2O$	200	82.08	–	14.82	3.10	1:0.21:0.26
$HfO(NO_3)_2 \cdot 2H_2O$	110	–	61.66	32.83	5.51	1:1.03:1.00
$HfO(NO_3)_2 \cdot 2H_2O$	200	–	77.82	19.76	6.39	1:0.50:0.63
$HfO(NO_3)_2 \cdot 2H_2O$	240	–	86.96	10.75	2.29	1:0.24:0.31

The equilibrium data obtained show that the zirconium and hafnium compounds differ somewhat in stability and in the character of their decomposition upon heating. Dehydration of zirconium oxynitrate dihydrate begins already at 40°. In the temperature range 40–120°, partial decomposition of the compound takes place; it proceeds slowly without a change in the crystalline structure. A certain increase in the percentage content of water in the residue is explained, in all probability, by the somewhat higher rate of removal of N_2O_5 and by the high molecular weight of N_2O_5 compared with H_2O. In the temperature range 120–200°, the decomposition process of zirconium oxynitrate dihydrate proceeds rapidly and is accompanied by destruction of the crystal lattice. At temperatures of 250–400°, the remaining small amounts of N_2O_5 (10 wt. %) and H_2O (1.5 wt. %) are removed, and monoclinic ZrO_2 is formed.

The hafnium compound possesses greater thermal stability; its decomposition also proceeds in stages, which are more clearly expressed. In the temperature range 60–80°, 0.5 molecule of water is removed; at 100–120° the monohydrate of hafnium oxynitrate is stable, the X-ray pattern of which differs somewhat from the X-ray pattern of the dihydrate; above 140° the rate of decomposition sharply increases and destruction of the crystalline structure of the substance takes place; at temperatures of 250–300°, the residues of N_2O_5 and H_2O are removed; above 400°, monoclinic HfO_2 is formed.

On the heating curves of the compounds, recorded with the Kurnakov pyrometer, three endothermic and one exothermic effects are clearly visible. The difference in thermal stability of the zirconium and hafnium oxynitrates is manifested most distinctly in the region of low temperatures. The first effect on the thermogram of $\mathrm{ZrO(NO_3)_2 \cdot 2H_2O}$ (60–100°) is associated with partial decomposition of the compound; the analogous effect (70–110°) for

Fig. 2. Curves of weight change on heating $ZrO(NO_3) \cdot 2H_2O$ (a) and $HfO(NO_3)_2 \cdot 2H_2O$ (b). Average heating rate 5-7°/min.

Figure 2: Fig. 2. Curves of weight change on heating $ZrO(NO_3) \cdot 2H_2O$ (a) and $HfO(NO_3)_2 \cdot 2H_2O$ (b). Average heating rate 5-7°/min.

$HfO(NO_3)_2 \cdot 2H_2O$ characterizes only the removal of the first molecule of water, which is confirmed by chemical analysis of the residues of the compounds (Table 2). The second effect, more clearly expressed for $HfO(NO_3)_2 \cdot 2H_2O$, covers the temperature ranges 150-180° and 160-200°, respectively, for zirconium and hafnium and is associated with further dehydration and decomposition of the compounds; according to chemical analysis data, in this region an unstable hafnium oxynitrate is formed with the ratio

$HfO_2 : N_2O_5 = 2 : 1$.

The existence of an analogous zirconium compound under these conditions is less probable. The last endothermic effect characterizes the complete decomposition of the zirconium and hafnium compounds, which occurs in the temperature ranges 186-200° and 210-240°, respectively. The exothermic effects are due to crystallization of monoclinic zirconium and hafnium oxides.

Fig. 2. Curves of weight change on heating $ZrO(NO_3)_2 \cdot 2H_2O$ (*a*) and $HfO(NO_3)_2 \cdot 2H_2O$ (*b*). Average heating rate 5-7°/min.

The results of the gravimetric method of analysis fully confirm the data obtained (Fig. 2). Thus, in the case of the zirconium compound, the change in sample weight on heating is expressed by a curve on which the existence of stable intermediate compounds is not observed. A decrease in the weight of the preparation occurs above 40°; in the interval 100-190° the greatest rate of decomposition is observed. The process is completed at 400° with the formation of ZrO_2; in this case the weight loss is 54.1%. According to gravimetric-analysis data, decomposition of hafnium oxynitrate dihydrate proceeds in stages. In the temperature interval 80-120°, 1 mole of H_2O is removed; in the region of 200° formation of digafnyl nitrate is observed, and finally, at 380-400° complete decomposition of the compound occurs.

Thus, the results of the thermal study, confirmed by X-ray phase and chemical analyses, make it possible to conclude that the dihydrates of zirconium and hafnium oxynitrates are thermally unstable compounds and decompose completely at 400°. Decomposition of the hafnium compounds proceeds in stages and is accompanied by formation of the monohydrate and of an unstable oxynitrate with the oxide ratio

$HfO_2 : N_2O_5 = 2 : 1$.

On heating $ZrO(NO_3)_2 \cdot 2H_2O$, no monohydrate is formed; the existence of an intermediate compound is less clearly expressed.

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