# General and Inorganic Chemistry

## Physicochemical transformations during synthesis of double K—Zr phosphates in a melt of potassium nitrate

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Double phosphates of K and Zr with three-dimensional and layered structure were synthesized in a melt of potassium nitrate in the temperature range of 300—550°C. The double phosphates were formed with participation of three components of a reaction mixture: $ZrOCl_2 \cdot 8H_2O$—$(NH_4)_2HPO_4$—$KNO_3$, in which potassium nitrate was both an active component of the reaction mixture and the reaction medium. The influence of the nature of the starting reagents on the composition of the reaction products and on the sequence and stoichiometry of the reactions proceeding in the reaction mixture were studied by thermogravimetry and mass-spectrometry.

**Key words:** phosphates of K and Zr, thermogravimetry, mass-spectrometry.

In view of their specific spatial structure, double K—Zr phosphates are promising for use as ionic conductors,[1,2] inorganic ion-exchangers,[3] and catalysts for acid-base and redox type reactions.[4] This stimulates a search for new Zr phosphate compounds as well as new methods of their synthesis. The use of salt melts as a reaction medium makes it possible to synthesize such compounds under comparatively mild conditions. The reactions in salt melts are employed for obtaining oxides,[5] mixtures of oxides,[6,7] and sulfides,[8] including highly dispersed oxides for ceramics[9] and catalytic processes.[10] Reactions in salt melts can yield products with a metastable structure or uncommon morphologic properties, for example, increased surface areas.[8]

The chemistry of phosphates in a medium of nitrate melts is poorly studied. The solubility of alkali metal phosphates and the acid-base transformations of phosphate ions in nitrate melts have been described.[11,12] The possibility of synthesis of double zirconium phosphates in a salt melt has been shown.[13] The reactions of phosphate ions and zirconium-containing compounds in a nitrate melt have also been studied.[14]

In this work, the sequence and stoichiometry of the reactions proceeding in a melt of $KNO_3$ containing Zr compounds and phosphates were studied by thermogravimetry and mass-spectrometry.

### Experimental

To prepare the reaction mixture, $ZrOCl_2 \cdot 8H_2O$ (chemically pure grade), $ZrO(NO_3)_2 \cdot 2H_2O$ (chemically pure grade), amorphous $ZrO_2 \cdot xH_2O$ obtained by precipitation with aqueous ammonia from a solution of $ZrO(NO_3)_2$, $(NH_4)_2HPO_4$ (chemically pure grade), $KH_2(PO_4)_3$ (chemically pure grade), and $K_3PO_4$ (chemically pure grade), as well as $KNO_3$ (reagent grade) as a reaction medium were used. A mixture of the starting reagents in the Zr:P:$KNO_3$ = 1:4:10 molar ratio was used as the reaction mixture[14] in the thermogravimetric and mass-spectroscopic studies.

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The phase composition of samples was monitored by X-ray phase analysis (XPA) method on a DRON-2 diffractometer with Cu-Kα radiation.

The chemical composition of samples was determined by atomic emission analysis.

The reaction dynamics was studied on a DERIVATOGRAPH Q-1500 D instrument.

The analysis of gaseous reaction products was carried out on a Gas trace A (FISONS Instruments) mass-spectrometer with a quadrupole analyzer (VG analyzer). The reaction mixture was heated at the rate of 1.5 deg $min^{-1}$ from room temperature to 550 °C. The gaseous reaction products were taken for analysis through a quartz tube heated to 453 K. Signals with $m/z$ = 18, 30, 32, 36, 44, 46, corresponding to $H_2O$, NO, $O_2$, HCl, $CO_2$, and $NO_2$, were registered.

## Results and Discussion

Previous results have shown[14] that double zirconium phosphates with layered and three-dimentional structure are formed in a melt of potassium nitrate in the temperature range of 330—550 °C, when $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2HPO_4$ are used as the starting reagents. It was found that at 330—430 °C, $KZr_2(PO_4)_3$ (ASTM — 25-1206) with the NASICON-type structure was the reaction product. Double phosphate $K_2Zr(PO_4)_2$ of the α-ZrP-type structure (ASTM — 28-857) was obtained at 500—550 °C.

The DTA curves describing the reaction of zirconium oxychloride with a potassium-sodium nitrate eutectic mixture (m.p. 220 °C) have been discussed previously.[13,15,16] Our data on the reaction of zirconium salt with $KNO_3$ (Fig. 1) showed no sharp maximum in the reaction rate. The increase in the rate of weight loss at 95—130 °C corresponds to dehydration and the beginning of thermal decomposition of $ZrOCl_2 \cdot 8H_2O$ (reaction (1)). This is confirmed by the presence of an endo-effect on the DTA curve in this temperature region.

$$ZrOCl_2 \cdot 8H_2O \rightarrow ZrO_2 + 7H_2O + 2HCl \qquad (1)$$

Endo-effects corresponding to the α—β-transition of crystal modification and melting of $KNO_3$ are registered on the DTA curve at 140 and 334 °C, respectively. The zirconium oxychloride fraction decomposes according to reaction (1) by the moment of $KNO_3$ melting (334 °C). Thus, the data of mass-spectrometry show that gaseous HCl evolves in an amount less than that corresponding to complete thermal decomposition of $ZrOCl_2 \cdot 8H_2O$. Hence, nonstoichiometric oxychloride $ZrO_{2-x}Cl_{2x}$ reacts with the melt, resulting in the absence of a sharp increase in weight loss in this temperature region.

$$ZrOCl_2 + 2KNO_3 \rightarrow ZrO_2 + 2NO_2 + 1/2O_2 + 2KCl \qquad (2)$$

According to data of mass-spectrometry, the peak of evolution of NO is registered at 180 °C; this can be accounted for by the interaction of $ZrOCl_2$ and $KNO_3$. In view of the absence of the peak corresponding to $O_2$ evolution at this temperature, one can suggest that the reaction of the $KNO_2$ admixture that is present in the nitrate proceeds in parallel.

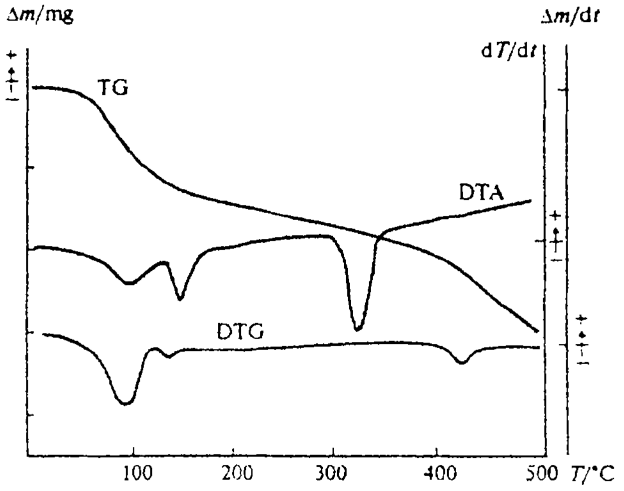

**Fig. 1.** The DTA, DTG, and TG curves for interaction in the $ZrOCl_2 \cdot 8H_2O—KNO_3$ mixture.

$$ZrOCl_2 + 2KNO_2 \rightarrow ZrO_2 + NO_2 + NO + 2KCl \qquad (3)$$

The effect of the admixture of nitrite on reactions in nitrate melts has been discussed in detail previously.[17] It is noteworthy that $KNO_2$ begins to react with the zirconium salt already at room temperature, and weight loss during reaction (3) is less than that in reaction (2).

The weight loss during the reaction of $ZrOCl_2$ and $KNO_3$ (63%) is intermediate between the calculated value for reactions (1), 61.5%, and (2), 78%; however, this does not contradict the occurrence of reaction (3). The product of the reaction between $ZrOCl_2 \cdot 8H_2O$ and $KNO_3$ at 500 °C is $ZrO_2$ with a large surface area (up to 200 $m^2$ $g^{-1}$).[13,16]

Endothermal peaks corresponding to the α—β-transition of the crystal modification (125 °C) and melting of $KNO_3$ (330 °C) as well as melting and decomposition of $NH_4H_2PO_4$ (193 °C) formed during the low-temperature thermal decomposition of $(NH_4)_2HPO_4$ are present on the low-temperature segment of the DTA curve describing the interaction of the $(NH_4)_2HPO_4—KNO_3$ binary mixture.

According to XPA data, potassium metaphosphate is the reaction product at 350 °C (reaction (4)).

$$KNO_3 + NH_4H_2PO_4 \rightarrow KPO_3 + NO + 1/2N_2 + 3H_2O \qquad (4)$$

Thus, the weight loss at temperatures below 350 °C is caused by decomposition of ammonium salts and a solid-phase reaction according to Eq. (4); this is confirmed by mass-spectrometry data. The ratio of the $NO/NO_2$ signals changes with increasing temperature and corresponds to the evolution of significant amounts of NO in the low-temperature region. In the temperature range of 300—600 °C, narrow peaks of weight loss are observed on the DTG curve at 527 and 565—570 °C; the latter is a superposition of two peaks. Interaction of metaphosphate and nitrate ions seems to occur in this temperature region, resulting in the formation of orthophosphate ions. According to XPA data, the reaction product contains a mixture of $K_3PO_4$ and $K_2P_2O_7$.

$$2PO_3^- + 2NO_3^- \rightarrow P_2O_7^{4-} + 2NO_2 + 1/2O_2 \qquad (5)$$

$$P_2O_7^{4-} + 2NO_3^- \rightarrow 2PO_4^{3-} + 2NO_2 + 1/2O_2 \qquad (6)$$

Solid-phase interacton between $(NH_4)_2HPO_4$ and $ZrOCl_2 \cdot 8H_2O$ yields well-crystallized zirconium pyrophosphate ($ZrP_2O_7$). At temperatures below 300 °C, the peaks on the DTG curve, which are accompanied by endo-effects on the DTA curve, correspond to thermal decomposition of the components of the reaction mixture. The peaks on the DTG curve in the 315—370 °C range correspond to solid-phase reactions, whose final product is $ZrP_2O_7$.

$$2(NH_4)_2HPO_4 + ZrOCl_2 \rightarrow \\ \rightarrow ZrP_2O_7 + 2HCl + 2H_2O + 4NH_3 \qquad (7)$$

The results of thermogravimetric study of interactions in the three-component $ZrOCl_2 \cdot 8H_2O$—$(NH_4)_2HPO_4$—$KNO_3$ mixture are presented in Fig. 2. An endo-effect peak is observed at 240 °C, which is not typical of above binary mixtures and is accompanied by a weight loss peak on the TG curve. Examination of mass-spectroscopic data showed that the weight loss was due to the evolution of $H_2O$ and small amounts of HCl, $NH_3$, and NO. One can suggest that the exo-effect peak at 240 °C corresponds to the reaction between $ZrOCl_2 \cdot 8H_2O$ and $KH_2PO_4$ (the last compound is formed from $(NH_4)_2HPO_4$ and $KNO_3$). However, this effect is absent during the reaction in the corresponding binary mixture studied by thermogravimetry. Thus, at this temperature the reaction between the components of the $ZrOCl_2 \cdot 8H_2O$—$(NH_4)_2HPO_4$—$KNO_3$ mixture seems to proceed according to the following scheme (8):

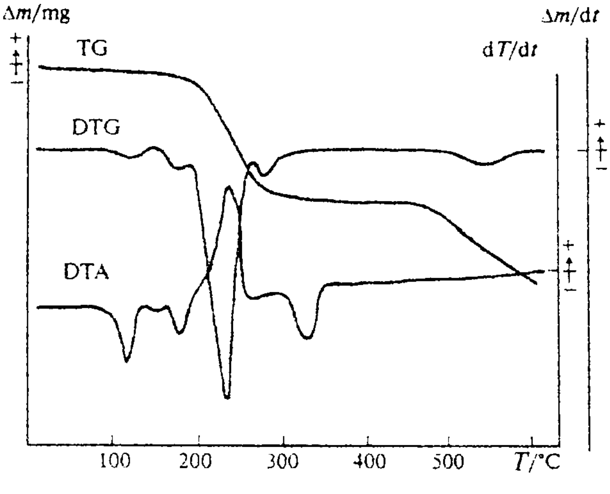

**Fig. 2.** The DTA, DTG, and TG curves for interaction in the three-component $ZrOCl_2 \cdot 8H_2O$—$(NH_4)_2HPO_4$—$KNO_3$ mixture.

$$2(NH_4)_2HPO_4 + ZrOCl_2 + KNO_3 \rightarrow \\ \rightarrow KHZr(PO_4)_2 + 4NH_3 + 2HCl + NO + O_2 + H_2O \quad (8)$$

It follows from XPA data that at 250 °C the $KHZr(PO_4)_2$ phase (ASTM — 28-0759), which decomposes in the temperature range 250—330 °C according to reaction (9), is present in the reaction products.

$$2KHZr(PO_4)_2 \rightarrow KZr_2(PO_4)_3 + KH_2PO_4 \qquad (9)$$

The reaction product at 330 °C is $KZr_2(PO_4)_3$ with a NASICON type structure (ASTM — 25-1206). According to data of chemical analysis, $KZr_2(PO_4)_3$ contains minor amounts of $KPO_3$ formed during thermal decomposition of $KH_2PO_4$.

At temperatures below 330 °C (m.p. of $KNO_3$) all reactions proceed in the solid phase and the reaction mixture is nonhomogeneous. Due to this fact, not only are the above interactions typical of binary and three-component mixtures possible, but also reactions caused by local overheating.

The endo-effects at 130, 190, 330 °C correspond to the α—β-transition of $KNO_3$, melting and decomposition of $NH_4H_2PO_4$, and melting of $KNO_3$, respectively.

Based on XPA data, formation of $K_2Zr(PO_4)_2$ with a α-ZrP type structure (ASTM — 28-857) occurs at temperatures above 400 °C; therefore, in the temperature range of 400—500 °C, the solid product contains a mixture of $KZr_2(PO_4)_3$ and $K_2Zr(PO_4)_2$.

$$Zr_2(PO_4)_3^- + PO_4^{3-} \rightarrow 2Zr(PO_4)_2^{2-} \qquad (10)$$

No gaseous products evolve during reaction (10). Consequently, weight loss in the high-temperature region is due to the reaction of excess phosphate ion with the nitrate melt, analogously to the above-considered reaction.

The nature of the starting reagents significantly affects the course of the reaction and the composition of the products. The thermal stability of the zirconium salts determines the composition of the zirconium-containing species at the temperature of the beginning of the reaction (240 °C). A comparison of thermogravimetric data for the three-component mixtures of the $ZrO_2$—$(NH_4)_2HPO_4$—$KNO_3$ and $ZrO(NO_3)_2 \cdot 2H_2O$—$(NH_4)_2HPO_4$—$KNO_3$ compositions with data presented in Fig. 2 showed that they are identical when $ZrO_2$ is used as the starting reagent. According to XPA data, the composition of the reaction products is the same in the temperature range studied. The use of $ZrO(NO_3)_2 \cdot 2H_2O$ as the starting reagent changes considerably the shape of the DTA and DTG curves (Fig. 3). Although the thermal decomposition of $ZrO(NO_3)_2 \cdot 2H_2O$ in air, like that of $ZrOCl_2 \cdot 8H_2O$, yields $ZrO_2$, it proceeds at higher temperatures. Thus, the endothermal peaks corresponding to dehydration and the beginning of decomposition of $ZrO(NO_3)_2 \cdot 2H_2O$, which is accompanied by weight loss peaks, are registered at 190 and 223 °C (130 and 160 °C for $ZrOCl_2 \cdot 8H_2O$).

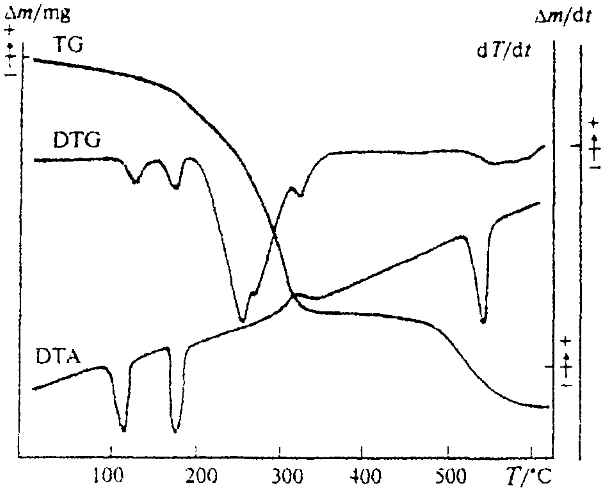

Fig. 3. The DTA, DTG, and TG curves for interaction in the three-component $ZrO(NO_3)_2 \cdot 2H_2O-(NH_4)_2HPO_4-KNO_3$ mixture.

$$ZrO(NO_3)_2 \cdot 2H_2O \rightarrow ZrO_2 + 2NO_2 + 1/2O_2 + 2H_2O \quad (11)$$

On the DTA curve for the three-component $ZrO(NO_3)_2 \cdot 2H_2O-(NH_4)_2HPO_4-KNO_3$ mixture (see Fig. 3) at temperatures below the m.p. of $KNO_3$, the exothermal effect peak is absent. This seems to be explained by the low extent of decomposition of zirconium oxynitrate in this temperature range, which makes it unable to take part in the solid-phase interaction (similarly to Eq. (8)) with the components of the reaction mixture. Thus, $KZr_2(PO_4)_3$ is formed after the melting of $KNO_3$ when ionic equilibria are attained in the melt.[14]

According to XPA data, the reaction products at 350 °C are $KZr_2(PO_4)_3$ and $KPO_3$. The last compound is formed in a significant amount and is difficult to separate due to its low solubility in water and acids. It follows from the results of chemical analysis that at 550 °C, regardless of the zirconium salt used, $K_2Zr(PO_4)_2$ is formed in the melt according to Eq. (10).

Thus, the nature of the zirconium salt affects considerably the pathway of the solid-phase reactions and the attainment of equilibria in a melt only in the low-temperature region and is not significant at the temperatures 450—550 °C.

Our results showed that the nature of the phosphate salt also markedly affects the reaction pathway and the composition of the products. Thus, according thermogravimetric data for the three-component $ZrOCl_2 \cdot 8H_2O-KH_2PO_4-KNO_3$ mixture, the exo-effect peak typical of a three-component reaction is absent at temperatures below 334 °C, *i.e.*, the use of $KH_2PO_4$ instead of the ammonium salt results in a change in the nature of the processes in the reaction mixture. When the ammonium salt, which readily melts and decomposes, is replaced by $KH_2PO_4$, formation of the double K—Zr phosphate with a NASICON type structure is observed only at temperatures above the m.p. of $KNO_3$ (334 °C) under the conditions of ionic equilibrium attained in the melt. Furthermore, the product is contaminated with $KPO_3$ formed in significant amounts during the thermal decomposition of $KH_2PO_4$. At 550 °C, $K_2Zr(PO_4)_2$ is the main reaction product regardless of the phosphate used.

Thus, the formation of double zirconium phosphate in a medium of $KNO_3$ in the low-temperature region (below 334 °C) is a solid-phase three-component reaction. At temperatures above 334 °C, potassium nitrate is both an active component of the reaction mixture and the reaction medium. The nature of the phosphates and the zirconium salts used significantly affects the reaction pathway and the composition of the products of solid-phase reactions at temperatures below 334 °C; in the high-temperature region the reaction pathway and the composition of the products are determined by the nature of the ionic equilibria in the melt[14] and are independent of the nature of the starting compounds.

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