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Abstract

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ON THE COMPOSITION AND PROPERTIES OF URANATES

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The investigations carried out ([1]) of the structures of uranates make it possible to consider the question of the influence of the nature of the cation on their composition and properties. The results of studies of the reactions of uranium trioxide and uranium dioxide–oxide with carbonates of alkali metals and with oxides or carbonates of certain divalent elements were published earlier ([2,3]). We have also studied the reactions of uranium dioxide–oxide with other salts of these elements and with lead oxide.

In the interaction of uranium oxides with nitrates, chlorides, and sulfates of sodium and potassium, as with carbonates, diuranates (or sometimes trihexauranates) are first formed. In the case of chlorides, in addition to uranates, chloruranates and uranyl chloride are obtained; with sulfates–uranyl sulfate. A further reaction between the diuranate and an excess of alkali salt is observed only in the case of nitrates (formation of Na_2UO_4). The addition even of a large excess of chloride or sulfate does not lead to the formation of monouranate. The alkalizing action of the salts studied decreases in the series: carbonate–nitrate –chloride–sulfate. With an excess of uranium oxides, polyuranates may form (up to lithium triuranate and potassium, rubidium, and cesium hexauranates). The structures of lithium triuranate and potassium trihexauranates are different. The peculiarity of the structure of potassium trihexauranate, stable only with large cation sizes, apparently explains the absence of analogous phases for sodium and lithium.

In contrast to the alkali elements, the formation of uranates in the interaction of U_3O_8 with chlorides of calcium, cadmium, and strontium begins with monouranates of calcium, cadmium (α-form), and structurally similar $SrUO_{3,4}$, which is then oxidized to $SrUO_4$ (β-form). At this point the interaction between U_3O_8 and an excess of chloride ends, whereas oxides and carbonates react with monouranates, giving orthouranates $Me^{II}_3UO_6$ (Ca, Sr, Ba, Cd) and $Me^{II}_2UO_5$ (Ca, Sr, Ba, Pb). Strontium and lead monouranates are capable of dissolving uranium trioxide (at temperatures of 1100 and 600°, respectively), forming phases whose X-ray patterns are almost indistinguishable from the X-ray patterns of the monouranates. In the case of the lead compound, raising the temperature to 800° leads to gradual decomposition of the phase formed, with

separation of monouranate. For strontium, annealing of solid solutions of UO_3 in β-$SrUO_4$ is accompanied by a rearrangement of the structure and formation of the phase $SrO \cdot 1.5$—$1.75\ UO_3$.

Thus, the initial products of the reaction of uranium dioxide–oxide or uranium trioxide with oxides and salts are usually uranates with hexagonal symmetry, since the mutual arrangement of uranium atoms in them is close to that present in the starting uranium oxides. This, in particular, explains the formation of hexagonal triuranates of magnesium and zinc in the interaction of uranium dioxide–oxide with the corresponding oxides.

Uranates of alkali elements, depending on their composition, undergo thermal decomposition either with loss of alkali oxide or with separation of uranium dioxide–oxide. In the series Li_2UO_4–Cs_2UO_4 the stability decreases in accordance with the increase in volatility of Me^{I}_2O. The lower thermal stabili-

the stability of rubidium and cesium monouranates explains the absence of polymorphism in them: decomposition occurs before the polymorphic transformation. Trihexauranates, characterized by large distances between uranyl-oxygen layers, are less stable (with the exception of rubidium tetrauranate). Of the alkali-element oxides, only lithium oxide, under definite conditions, is capable of giving solid solutions of composition $(Li, U)O_{2\pm x}$ with uranium oxides. Decomposition of lithium uranate in vacuum proceeds according to the scheme: $Li_2UO_4 \rightarrow LiUO_3 \rightarrow (Li, U)O_{2\pm x}$ (with loss of lithium oxide). By contrast, in the case of divalent elements the decomposition of uranates is usually accompanied by the formation of solid solutions $(Me^{II}, U)O_{2\pm x}$ with the fluorite structure (if the volatility of $Me^{II}O$ is not too great).

Consequently, the thermal stability of uranates and the type of their thermal decomposition are determined, on the one hand, by the volatility of the basic oxide (or its thermal stability), and, on the other hand, by the minimum amount of this oxide required to stabilize the hexavalent state of uranium. The decomposition process is also substantially affected by the ability of basic oxides to form solid solutions with uranium oxides.

The composition of the products of reduction of uranates by hydrogen depends on the stability of the corresponding compounds of uranium of lower valence (V and IV) and of the given element. As we have established, lithium and cesium monouranates, even at low temperature (350–400°), are reduced by hydrogen to uranium oxides UO_{2+x} (the reactions are practically irreversible). For reduction by hydrogen of sodium and potassium diuranates and potassium and rubidium monouranates, a higher temperature is necessary (400–550°); moreover, reduction of the diuranates first proceeds without destruction of the uranate structure (phases $Me_2U_2O_{7-x}$). At the next stage of reduction, sodium and potassium uranates(V) of composition $Me^{I}UO_3$ (perovskite structure) are formed. The reduction product of rubidium monouranate has the composition Rb_xUO_3 ($x \sim 0.85$). The corresponding lithium uranate(V) is formed only during thermal decomposition of Li_2UO_4 in vacuum. A further increase in the reduction

temperature leads to the formation of uranium dioxide. In the reduction of more acidic uranates (for example, $K_2U_3O_{10}$), uranate(V) and UO_{2+x} are first obtained. Uranates(V) are more stable in the presence of free alkali-element hydroxide. Uranates(V) readily dissolve in oxidizing acids, and more slowly in dilute hydrochloric and sulfuric acids. On calcination in air they are oxidized, giving the corresponding uranates. In contrast to "tungsten bronzes," uranates(V) are characterized by a narrow homogeneity range and greater chemical activity.

Reduction of the uranates of alkaline-earth metals begins at a higher temperature ($> 600°$) and is accompanied by the formation of phases $Me^{II}UO_{4-x}$ without change (Ca, Ba) or with change (Sr) in the structure of the initial uranate. By oxidation of $SrUO_{4-x}$ below 700°, a metastable α-modification of $SrUO_4$ can be obtained. A further increase in the reduction temperature leads to the formation of cubic phases with the fluorite structure.

Reduction of zinc and cadmium uranates is accompanied by the liberation of uranium oxides and metallic zinc and cadmium.

In potentiometric titration of uranyl salts with alkalis, irrespective of the nature of the hydroxide used, inflection points on the curves were observed upon addition of 1; 1.5; 2; 2.28; 2.5 and 3 moles of $Me^{I}OH$ per 1 mole of uranyl nitrate, which corresponds to the formation of the following compounds: $UO_2(OH)NO_3$ (pH 2.5-3.5), $(UO_2)_2(OH)_3NO_3$ (pH 3.5-5.0), $UO_2(OH)_2$ (pH 4.0-5.5), $Me_2U_7O_{22}$ (pH 6.0-6.5), $Me_2U_4O_{13}$ (pH 7.0-9.0), and $Me_2U_2O_7$ (pH 9.0-11.0).

As a result of chemical and X-ray diffraction analysis of precipitated sodium uranates obtained at different pH values (the adsorbed alkali was washed off with alcohol), the existence of two phases was established:

$Na_2O \cdot 2\text{–}4UO_3$ with the structure of $CaUO_4$, and $Na_2O \cdot 4\text{–}7UO_3$ with the structure of potassium trihexauranate. An X-ray study of suspensions of precipitated sodium and potassium uranates in 10% solutions of the corresponding hydroxides showed that monouranates of the alkali elements are not formed in an aqueous medium.

The precipitates obtained under identical conditions by the action of an excess of the corresponding hydroxide on a uranyl salt solution, after washing with water until complete removal of hydroxyl ions, had the following approximate composition: $Li_2O \cdot 2.5UO_3$; $Na_2O \cdot 2.5UO_3$; $K_2O \cdot 3UO$; $Rb_2O \cdot 4U_3O_3$; $Cs_2O \cdot 4\text{–}6UO_3$. When the precipitated lithium uranate is washed with hot water, almost complete hydrolytic decomposition of the preparation may occur. Products analogous in composition were also obtained as a result of hydrolysis of the corresponding anhydrous monouranates (boiling a weighed portion of uranate with water in a flask with a reflux condenser for several hours). Thus, in the case of sodium uranate, hydrolysis stops at the formation of compounds belonging to the first homogeneous phase.

When a uranyl nitrate solution was titrated with calcium, strontium, and barium hydroxides, inflection points on the titration curves were observed upon the addition of 0.75; 1; 1.16; 1.25; 1.33; 1.5; and 2 moles of hydroxide per 1 mole of uranyl nitrate, which corresponds to the formation of $(UO_2)_2(OH)_3NO_3$, $UO_2(OH)_2$, MeU_6O_{19}, MeU_4O_{13}, MeU_3O_{10}, MeU_2O_7, and $MeUO_4$. Addition of 0.5 mole of hydroxide caused an intensification of the color of the solution (formation of $UO_2(OH)NO_3$). As a result of studying the composition of precipitated calcium uranates obtained at the indicated reagent ratios (standing for two weeks, washing with small amounts of ice water), the formation was established of somewhat hydrolyzed calcium monouranate (pH > 11) and diuranate (pH 11–10) with increased parameters a and c, owing to the entry of OH ions and water molecules into the lattice. At pH 9.5–6.5, uranates with a Ca : U ratio of 4–7 were formed. The products of their calcination (500°) constitute a single phase with a structure close to U_3O_8 but not identical to it (a solid solution based on U_3O_8).

Dehydration of precipitated uranates proceeds in the range 150–250° and, with the close structure of the hydrated and anhydrous uranates, is accompanied by a change in the lattice parameters (sodium and potassium diuranates, potassium triuranate, calcium mono- and diuranate). Heating precipitated sodium uranates (with $Na_2O : UO_3$ 1 : 4) is accompanied by the formation (750°) of a metastable phase, similar in its structure to the diuranate (with $a = 3.91$ and $c = 17.12$), but with a noticeably smaller volume (the presence of a large number of defects in the structure). Upon further heating it decomposes into diuranate and uranium oxide-oxide.

Anhydrous uranates become hydrated (in the cold and on boiling) only in the case where their hydrolysis proceeds simultaneously. Otherwise they do not add water. Thus, for example, 6-hour boiling of anhydrous potassium tetrauranate was not accompanied by its hydration, and all the water was readily washed off with alcohol.

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