## Alkali-Ion-Catalyzed Transformation of Two Linear Uranyl Phosphonates into a Tubular One

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Uranyl ion  $UO_2^{2+}$  is widely known for its photochemical and photocatalytic redox behavior<sup>1-5</sup> and for its interesting luminescence properties<sup>6,7</sup> and rich spectroscopy.<sup>8-10</sup> However, seldom is this linear ion thought to be capable of forming extended lattices of a variety of covalently bound structure types<sup>11,12</sup> and, least of all, of undergoing transformations of these structures at room-temperature. Several recent investigations into how the uranyl ion interacts with alkyl- and arylphosphonic anions has led to the synthesis of a variety of structure types, linear-chain, layered, and tubular.<sup>13-16</sup> This is somewhat surprising given the fact that the uranyl ion can bind ligands only in its equatorial plane. This axial anisotropy should lead to a limited number of possibilities in which this cation can interact with anionic ligands to form extended lattices compared with the isotropic cations of the  $M^{x+}$  type, but the opposite is true.

Very recently, we have synthesized two linear-chain structures, *cis*- $\alpha$ -uranyl phenylphosphonate ( $\alpha$ -UPP), [UO<sub>2</sub>(HO<sub>3</sub>-PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sub>2</sub>·8H<sub>2</sub>O,<sup>14</sup> and *trans*- $\beta$ -uranyl phenylphosphonate ( $\beta$ -UPP), [UO<sub>2</sub>(HO<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)]·3H<sub>2</sub>O<sup>13</sup> (Figure 1). Single crystals of  $\alpha$ -UPP slowly transformed in air and at room temperature and moderate humidity into  $\beta$ -UPP.<sup>13</sup> A mechanism for explaining the transformation was suggested, and it involved breaking of the U–O<sub>phosphonate</sub> bond and a rotation of the phenylphosphonate group about another, unbroken U–O<sub>phos-</sub> phonate bond.

Upon attempting to investigate the ion-exchange properties of the two new compounds  $\alpha$ -UPP and  $\beta$ -UPP, we have found that in the presence of the sodium or calcium ions in the form of NaCl, NaH(O<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>), or CaCl<sub>2</sub> in an aqueous environment, both the linear-chain  $\alpha$ -UPP and  $\beta$ -UPP transformed into another form, which has been structurally characterized earlier,<sup>17</sup> the tubular UO<sub>2</sub>(O<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)•0.7H<sub>2</sub>O ( $\gamma$ -UPP). (Figure 2). The transformation was followed by X-ray powder patterns (Figure 3) which showed that a ground sample of  $\alpha$ -UPP transformed

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**Figure 1.** Structures of  $\alpha$ -UPP and of  $\beta$ -UPP (view along the infinite linear chains).



Figure 2. Transformations occurring between three uranyl phenylphosphonates at room-temperature conditions.



**Figure 3.** XRD powder patterns monitoring the transformation of *cis*- $\alpha$ -UPP into tubular  $\gamma$ -UPP.

into  $\gamma$ -UPP within 3 h, whereas a ground sample of  $\beta$ -UPP transformed under identical conditions into  $\gamma$ -UPP in approximately 7 h. Only a very small trace of the sodium ion was detected in the produced  $\gamma$ -UPP by atomic absorption spectroscopy. The transformation proceeded only in an acidic

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<sup>(1)</sup> Rabinowitch, E.; Belford, R. L. Spectroscopy and Photochemistry of Uranyl Compounds; Pergamon Press: Oxford, U.K., 1964.

environment at pH 2–4; in a basic environment as in the presence of diluted NaOH or  $Na_2(O_3PC_6H_5)$ , an undefinable product resulted.

This interesting result raised the question of whether a solidstate reaction was taking place during which six neighboring infinite linear chains of  $\alpha$ -UPP (or  $\beta$ -UPP) would merge together into an infinite tube of  $\gamma$ -UPP, or whether the original lattices of  $\alpha$ -UPP and  $\beta$ -UPP disassembled into uranyl and phenylphosphonate ions and reassembled to form a new lattice of  $\gamma$ -UPP. For this purpose, the transformation was carried out in the presence of NaHO<sub>3</sub>PC<sub>6</sub>D<sub>5</sub>,<sup>18</sup> where the total amount of deuterated phenylphosphonic anions in the solution was the same as the total amount of protonated phenylphosphonic anions present in the ground crystals of  $\alpha$ -UPP.<sup>19</sup> The formed compound,  $\gamma$ -UPP, was recovered and dissolved in diluted HF, and the +FAB/DP mass spectrum was acquired. The ratio of the peaks at 159 atomic mass units (amu) and at 164 amu in the +FAB/ DP spectrum corresponding to the masses of  $H_3O_3PC_6H_5^+$  and  $H_3O_3PC_6D_5^+$ , respectively, was approximately 1.2:1.0. This indicates that a significant degree of incorporation of the deuterated phenylphosphonic anion took place during the transformation. Thus it is possible to exclude the fusion of infinite chains into the infinite tubes. Disassembling of the uranyl and phenylphosphonate ions of  $\alpha$ -UPP and  $\beta$ -UPP is more likely taking place followed by reassembling of the ions in the form of  $\gamma$ -UPP. The initial deprotonation of the phenylphosphonic anion coordinating the uranyl ion in the solid lattice apparently leads to its increased solubility, and a dynamic equilibrium is established between the solid and liquid phases:

$$UO_{2}(HO_{3}PPh)_{2} \cdot xH_{2}O \xrightarrow{Na^{+}(l)} UO_{2}^{2^{+}} + 2HO_{3}PPh^{-}(l) \xrightarrow{\sim} \alpha$$
-UPP or  $\beta$ -UPP  
$$UO_{2}(O_{3}PPh) + H_{2}O_{3}PPh (1) \xrightarrow{\gamma}$$
-UPP

Apparently,  $\gamma$ -UPP is thermodynamically more stable than either  $\alpha$ -UPP or  $\beta$ -UPP, and that is why the dynamic equilibrium eventually transfers all the uranyl ions and one-half the phenylphosphonate anions through the dissolved state into the  $\gamma$ -UPP phase. The slower reaction rate of  $\beta$ -UPP compared to that of  $\alpha$ -UPP is due to a slower disassembling of the  $\beta$ -UPP lattice as the phenyl rings of neighboring chains in  $\beta$ -UPP interlock each other (Figure 1), whereas the structure of  $\alpha$ -UPP is formed of easily penetrable and separable hydrophilic and hydrophobic regions. Attempts to carry out a similar transformation in solvents with a dielectric constant lower than that of water failed, particularly due to the low solubility of most available sodium salts in these solvents.

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<sup>(18)</sup> Protonated phenylphosphonic acid was purchased from Aldrich, and deuterated acid was prepared from  $C_6D_5Br$  according to the following: Tavs, P. *Chem. Ber.* **1970**, *103*, 2428–2436.

<sup>(19)</sup> A 50 mg (0.31 mmol) amount of deuterated phenyphosphonic acid was dissolved in 10.5 mL of deionized water, and 1.50 mL of 0.202 M NaOH (0.303 mmol) was added. The pH of the solution was 3.5; thus the solution contained mostly NaHO<sub>3</sub>PC<sub>6</sub>D<sub>5</sub> and a small amount of H<sub>2</sub>O<sub>3</sub>PC<sub>6</sub>D<sub>5</sub>. Next, 100 mg of  $\alpha$ -UPP (0.148 mmol of U and 0.297 mmol of P) was gently ground with a spatula and added into the solution and magnetically stirred. Samples of the suspension were pipeted and filtered after 45, 100, and 200 min, and they were filtered, throughly washed with deionized water and dried, in air. X-ray diffraction powder patterns monitoring the relative ratio of  $\alpha$ -UPP and  $\gamma$ -UPP were measured on double-sided tape, and after 200 min, only  $\gamma$ -UPP was present in the suspension (Figure 3). This sample was dissolved in an HF solution and analyzed by +FAB mass spectrometry.