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Comparison of Reactivity Based on Intercalation and Host Lattice Reconstruction. Two Routes for the Conversion of the Lamellar Solid Hydrogen Uranyl Phosphate to a Lamellar Hydrate of Uranyl Phosphate

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The solid-state structural changes accompanying intercalation can be profound and have been used to analyze interactions of guest species with host lattices.[1] We and others have studied hydrogen uranyl phosphate (HUP), HUO_2PO_4, and demonstrated that the lamellar solid readily undergoes intercalative ion-exchange reactions, eq 1.[2-6] Typically, the protons residing between the

$$(1/n)M^{n+} + HUO_2PO_4 \rightarrow M_{1/n}UO_2PO_4 + H^+ \tag{1}$$

$(UO_2PO_4)_n^{n-}$ sheets can be exchanged simply by slurrying the HUP powder in an aqueous solution containing the ion to be intercalated.

It occurred to us that use of UO_2^{2+} as the intercalant in eq 1 would lead to formation of uranyl phosphate (UP), $(UO_2)_3(PO_4)_2$. Furthermore, the report[7] that UP can be prepared from an aqueous HUP slurry by thermal decomposition, eq 2, provided us with a

$$3HUO_2PO_4 \rightarrow H_3PO_4 + (UO_2)_3(PO_4)_2 \tag{2}$$

novel opportunity to compare two pathways to the same product. We report herein that HUP can be quantitatively converted by intercalation (eq 1) or host lattice reconstruction (eq 2) to a common lamellar hydrate of UP; both reactions are reversible at room temperature. Moreover, an Arrhenius treatment of calculated rates for the forward reactions supports the notion that they proceed by quite different mechanisms.

Intercalation was typically effected by slurrying 300 mg of HUP powder[7] in 20 mL of a 0.5 M aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ for several hours. Elemental analysis is consistent with a formula of $(UO_2)_3(PO_4)_2 \cdot 8H_2O$.[8a]

A Debye–Scherrer X-ray powder diffraction pattern[4,9] of the poorly crystalline solid is dominated by a phase that closely matches that previously reported for $(UO_2)_3(PO_4)_2 \cdot 8H_2O$.[10] Although we have been unable to obtain single crystals of the intercalated solid, its structure can be inferred from its synthesis by ion exchange and its X-ray data, which can be indexed on the basis of a tetragonal cell with $a = 6.93$ Å, comparable to its value in HUP, and $c = 11.1$ Å, expanded from an interlamellar spacing of 8.69 Å in HUP.[2] These results imply that $(UO_2)_3(PO_4)_2 \cdot 8H_2O$, like the family of $M^{n+}{}_{1/n}UO_2PO_4 \cdot 3H_2O$ compounds,[11] is a structural relative of HUP with UO_2^{2+} ions occupying sites between the $(UO_2PO_4)_n^{n-}$ sheets. The unit cell expansion of 2.4 Å corresponds to the van der Waals diameter of the uranyl oxygen atoms[12] and suggests that the principal rotation axes of the interlamellar UO_2^{2+} ions lie parallel to the sheets.

Unlike HUP, the intercalated solid exhibits only weak photoluminescence (PL) at 295 K and has a lifetime of 5–10 μs, considerably shorter than the HUP value of ~450 μs.[2] The quenching may result from host-to-guest energy transfer,[2-4] with the interlamellar UO_2^{2+} guest ions serving as efficient centers for nonradiative decay.

Rates for the intercalation reaction were estimated between 0 and 25 °C (above which HUP begins to decompose, vide infra) by determining the time needed for characteristic HUP reflections to disappear from the powder pattern; rates (mol/s) were independent (±10%) of slurry concentration (1.0–20.0 g/L) and UO_2^{2+} ion concentration (0.5–1.0 M). Figure 1 presents an Arrhenius plot of the data, yielding an apparent activation energy (E_a) of 12 ± 2 kcal/mol and an ln A value of 5 ± 2.

Having prepared uranyl phosphate by intercalation, eq 1, we then synthesized it by slurrying HUP in water (typically, 100–1000 mg in 20 mL) at elevated temperatures. Loss of PL intensity from the slurry provided a convenient means for following the reaction.[13] The solids isolated after heating were also analyzed to be $(UO_2)_3(PO_4)_2 \cdot 8H_2O$[8b] and had virtually identical IR spectra,[8a] X-ray powder diffraction data,[9] and PL properties with the intercalated samples. During the reaction, the pH of the system dropped from ~7 to 3.5, consistent with loss of H_3PO_4 from the lattice, eq 2.

For kinetic analysis, we arbitrarily used the time needed to reach 25% of the initial PL intensity as a measure of reaction rate;[14] typical PL decay curves are shown in the inset of Figure 1. An Arrhenius treatment of the data in Figure 1 (45–75 °C) yields an apparent E_a value of 30 ± 2 kcal/mol and an ln A value of 28 ± 3. The rate of decomposition was found to increase by ~20% when neutral pH was maintained throughout the reaction and to decrease by ~30% when the reaction was performed in 0.001 M H_3PO_4, but the apparent E_a values were unaffected.

Samples of UP prepared by the thermal decomposition reaction revert to HUP if left in the mother liquor at room temperature for 48 h.[15] The HUP thus recovered was somewhat less crystalline than the unreacted samples but had equally intense PL and no UP present in the X-ray patterns. Air-dried samples of UP, obtained either by decomposition or intercalation, return to HUP at similar rates over a 3-day period when stirred in 0.01 M H_3PO_4 at 25 °C.

Although intercalation and host lattice reconstruction yield the same solid, the difference in calculated Arrhenius parameters is striking and consistent with a change in mechanism. The larger E_a and ln A values found for the thermal decomposition of HUP might arise from complete dissolution and subsequent repreci-

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[7] Weigel, F.; Hoffman, G. *J. Less-Common Met.* **1976**, *44*, 99. Our powders were hand-ground with an agate mortar and pestle immediately before use. The mean particle size of the resulting powder was typically 2.5 μm, as determined by quasi-elastic light scattering, as described in: Yu, H. *J. Res. NBS* **1981**, *86*, 571.

[8] (a) Anal. (Galbraith) Calcd for $H_{16}O_{22}P_2U_3$: H, 1.40; P, 5.42; U, 62.41. Found: H, 1.40; P, 5.37; U, 61.80. IR (Nujol) 1625 (m) (H_2O), 1165 (s) (PO_4^{3-}), 1060 (vs) (PO_4^{3-}), 980 (m) (PO_4^{3-}), 930 (vs) (UO_2^{2+}), 850 (m) (UO_2^{2+}). (b) Anal. Calcd (see above). Found: H, 1.45; P, 5.33; U, 61.99.

[9] X-ray powder diffraction reflections: d (Å) = 11.09 (s), 6.86 (m), 5.56 (m), 4.59 (s), 3.71 (m), 3.28 (s), 2.96 (s), 2.17 (w), 2.07 (w), 1.40 (m), 1.18 (ms), 1.13 (ms). A weak, broad line also appears at $d = 4.21$ Å, indicating the presence of a small amount (<5%) of tetrahydrate in air-dried samples.

[10] Pavkovic, N.; Markovic, M. *Radiochim. Acta* **1983**, *34*, 127. The reported powder pattern is more complex than ours but can be indexed on the basis of a cell that is slightly orthorhombically distorted from the tetragonal cell described in the text.

[11] Pavkovic, N.; Markovic, M.; Kojic-Prodic, B. *Croat. Chem. Acta* **1982**, *55*, 405.

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[13] When the reaction is monitored by powder X-ray diffraction, it is found to proceed through an initial loss of crystallinity of HUP, accompanied by loss of PL intensity. Our results, which yield rates for the disappearance of HUP, do not permit us to say whether direct conversion of HUP to UP occurs, because the pattern of UP does not begin to appear until shortly before the PL intensity reaches a minimum; the UP pattern then grows in intensity and sharpens as the reaction proceeds. When HUP is heated above ~75 °C, reflections are observed that indicate the presence of increasing amounts of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$. The octahydrate, like HUP, can be completely converted to the tetrahydrate by stirring the solid in boiling water for 5 h: Pham-Thi, M.; Colomban, P. *J. Less-Common Met.* **1985**, *108*, 189. DSC traces of the octahydrate reveal a phase change at 110 °C, resulting in the tetrahydrate phase, as verified by X-ray data.

[14] This corresponds to substantial structural conversion; similar E_a values are found if 50% and 10% of the initial PL intensity are used to characterize the reaction rate or if reaction rates are based on the disappearance of HUP from the powder pattern of the solid product.

[15] The reaction of a lower hydrate of UP with H_3PO_4 was found to be a temperature-dependent equilibrium. See: Weigel, F. in *Handbook on the Physics and Chemistry of the Actinides*; Freeman, A. J., Keller, C., Eds.; Elsevier: Amsterdam, 1985; p 243.

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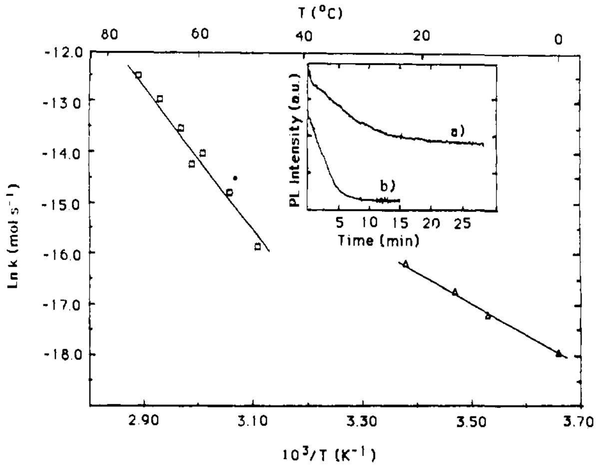

Figure 1. Arrhenius plots for the conversion of hydrogen uranyl phosphate to uranyl phosphate by thermal decomposition in water (squares) and by stirring with UO_2^{2+} ions (triangles). Decomposition experiments were conducted with 200 mg of HUP in 20 mL of triply distilled H_2O; for the intercalation reaction, 300 mg of HUP and a 0.5 M $UO_2(NO_3)_2$ solution were used. Each data point is the average of 2–4 runs. Slurries were stirred vigorously at temperatures maintained with an oil bath to ±0.5 °C. Inset: Representative PL decay curves for HUP decomposition at (a) 60 °C and (b) 70 °C. The initial PL intensities have been offset for clarity.

pitation of the solid. Alternatively, the reaction's reversibility suggests a "self-intercalation" mechanism, in which the elevated temperature increases the solubility of HUP. The uranyl ions thus liberated are then free to exchange with protons in undissolved HUP to give the observed products. The significance of the Arrhenius parameters is being assessed by characterization of related systems in our laboratories.

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Registry No. HUO_2PO_4, 61156-01-2; $(UO_2)_3(PO_4)_2{\cdot}8H_2O$, 84934-15-6.

Chemistry of *cis,syn*-Tricyclo[6.4.0.0^{2,7}]dodeca-3,5,9,11-tetraene, a New 4n Dimer of Benzene

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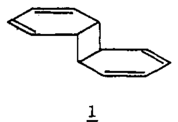
There is substantial theoretical interest[2] in the benzene 4n cyclodimer subset (**1**–**3**) of the $(CH)_{12}$ series of isomers. Among the three members of this subset, only the *anti-o,o'*-dibenzene (**1**) has been prepared.[3] We wish to report the synthesis and some novel chemical reactions of a new addition to this energy-rich class of molecules, *cis,syn*-tricyclo[6.4.0.0^{2,7}]dodeca-3,5,9,11-tetraene (**2**) or *cis,syn-o,o'*-dibenzene.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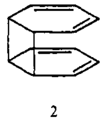
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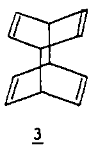
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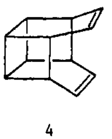
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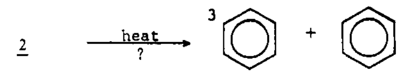
Recently, we had synthesized a pentacyclic dimer of benzene **4**[4] and found that **4** undergoes a facile thermal rearrangement at moderate temperature to **2** with the formation of benzene as the only other product. Thermolysis of **4** at 40 °C in pentane (6.4 × 10^{-3} M) under argon for 9.7 days, followed by flash chromatography over silica gel and cautious removal of the solvent, afforded **2** as colorless crystals with a characteristic camphor-like odor in 16% yield (isolated): mp 45–46 °C; MS found, *m/z* 156.0928; UV (C_6H_{12}) λ_{max} 240 nm (ϵ 4900); IR (C_6D_{12}) 3034, 2956, 2925, 2873, 2856, 1712 cm^{-1}; ^{1}H NMR (C_6D_{12}) δ 3.51 (br s, 4 H), 5.32 (br d, 4 H), 5.64 ppm (dd, J = 7.5 and 2.5 Hz); ^{13}C NMR (C_6D_{12}) δ 42.62, 123.85, 124.98.

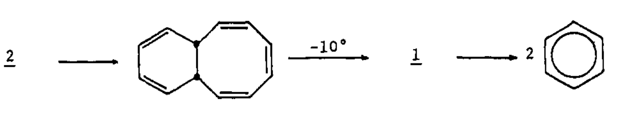
Since **1** is known to exhibit a half-life of 5.75 h at 40 °C,[3a] our results clearly indicate that **2** is thermally more stable than its cis,anti isomer **1**. It is surprising that, on the basis of thermochemical calculations,[5] **2** is the less stable isomer thermodynamically due to the unfavorable overlapping interactions between the two cyclohexadiene rings. However, Gleiter has shown that the through-bond interactions between the two isolated π-systems may be more important than their through-space interactions, suggesting that the HOMO of **1** may be actually higher than that of **2**.[2d,e] Our finding that the UV maximum of **2** (240 nm) is substantially blue-shifted from that of **1** (266 nm)[3a] is in agreement with his prediction. It is conceivable that the higher thermokinetic stability of **2** may be related to its lower HOMO level. The kinetics of thermolysis of **2** was then investigated in the temperature range 61.0–80.1 °C, and the following parameters were obtained: $\Delta H^{\ddagger}$ = 22.5 ± 1.3 kcal·M^{-1} and $\Delta S^{\ddagger}$ = −14.0 ± 2.2 eu.

Since the direct thermal dissociation of **2** into two molecules of benzene is highly exoergic but symmetry forbidden as a concerted process,[6] it is surprising that the reaction proceeds with such a highly negative activation entropy. The observation suggests that the reaction may proceed via a spin-forbidden transition state (pathway 1)[7,8] or via a metastable intermediate formed in a concerted process (pathway 2). The former pathway involves the formation of a molecule of benzene in its triplet state. The ΔG of the thermolysis of **2** may be estimated from thermochemical data to be approximately −73 kcal·M^{-1}.[5,9] This pathway is possible since the amount of energy available, the sum of ΔG and $\Delta G^{\ddagger}$, exceeds the triplet energy of benzene, 84.3 kcal·M^{-1}.[10] The latter pathway involves the disrotatory opening of the cyclobutane ring

Pathway 1



Pathway 2



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[1] This work is dedicated to Professor George H. Büchi on his 65th birthday.

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