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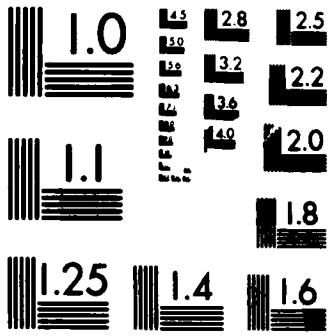

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# Comparison of Reactivity Based on Intercalation and Host Lattice Reconstruction. Two Routes for the Conversion of the Lamellar Solid Hydrogen Uranyl Phosphate to a Lamellar Hydrate of Uranyl Phosphate

by

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The lamellar solid hydrogen uranyl phosphate (HUP), $HUO_2PO_4$, can be quantitatively converted to a lamellar hydrate of uranyl phosphate, (UP), $(UO_2)_3(PO_4)_2 \cdot 8H_2O$, by two routes: an intercalative ion-exchange reaction with aqueous $UO_2^{2+}$ ions and thermal decomposition in an aqueous slurry. An X-ray powder pattern of the product can be indexed in tetragonal symmetry with an interlamellar spacing of 11.1 Å, expanded from a value of 8.69 Å in HUP. Conversion of HUP to UP is accompanied by a drastic diminution in photoluminescence lifetime and intensity. Arrhenius parameters derived from the rates of the intercalation and thermal decomposition reactions indicate that they proceed by quite different mechanisms: the intercalation reaction proceeds with an apparent activation energy, $E_a$, of 12 ± 2 ~~kcal/mol~~ and a ~~ln A value~~ of 5 ± 2; thermal decomposition, involving reconstruction of the host lattice, is characterized by an $E_a$ value of 30 ± 2 kcal/mol and a ln A value of 28 ± 3. Samples of UP, obtained by either method, can be converted back to HUP by the action of dilute phosphoric acid in an aqueous slurry at room temperture. Possible mechanisms for these reactions are discussed.

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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

$$(1/n)\ M^{n+} + HUO_2PO_4 \text{ --> } M_{1/n}UO_2PO_4 + H^+ \qquad (1)$$

residing between the $(UO_2PO_4)_n^{n-}$ 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 novel

$$3\ HUO_2PO_4 \text{ -----> } H_3PO_4 + (UO_2)_3(PO_4)_2 \qquad (2)$$

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 $\underline{a}$ = 6.93 Å, comparable to its value in HUP, and $\underline{c}$ = 11.1 Å, expanded from an interlamellar spacing of 8.69 A 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 usec, considerably shorter than the HUP value of ~450 usec.[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 $25^0$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/sec) were independent ($\pm$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 $\pm$ 2 kcal/mol and ln A value of 5 $\pm$ 2.

Having prepared uranyl phosphate by intercalation, eq. 1, we then synthesized it by slurrying HUP in water (typically, 100 to 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 to 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 fig. 1. An Arrhenius treatment of the data in fig. 1 (45-75$^0$C) yields an apparent $E_a$ value of 30 $\pm$ 2 kcal/mol and a ln A value of 28 $\pm$ 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 hours. The HUP thus recovered was somewhat less crystalline than 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$^o$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 reprecipitation 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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7. Weigel, F.; Hoffman, G. J. Less-Common Mets. **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 um, as determined by quasielastic 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) and 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.

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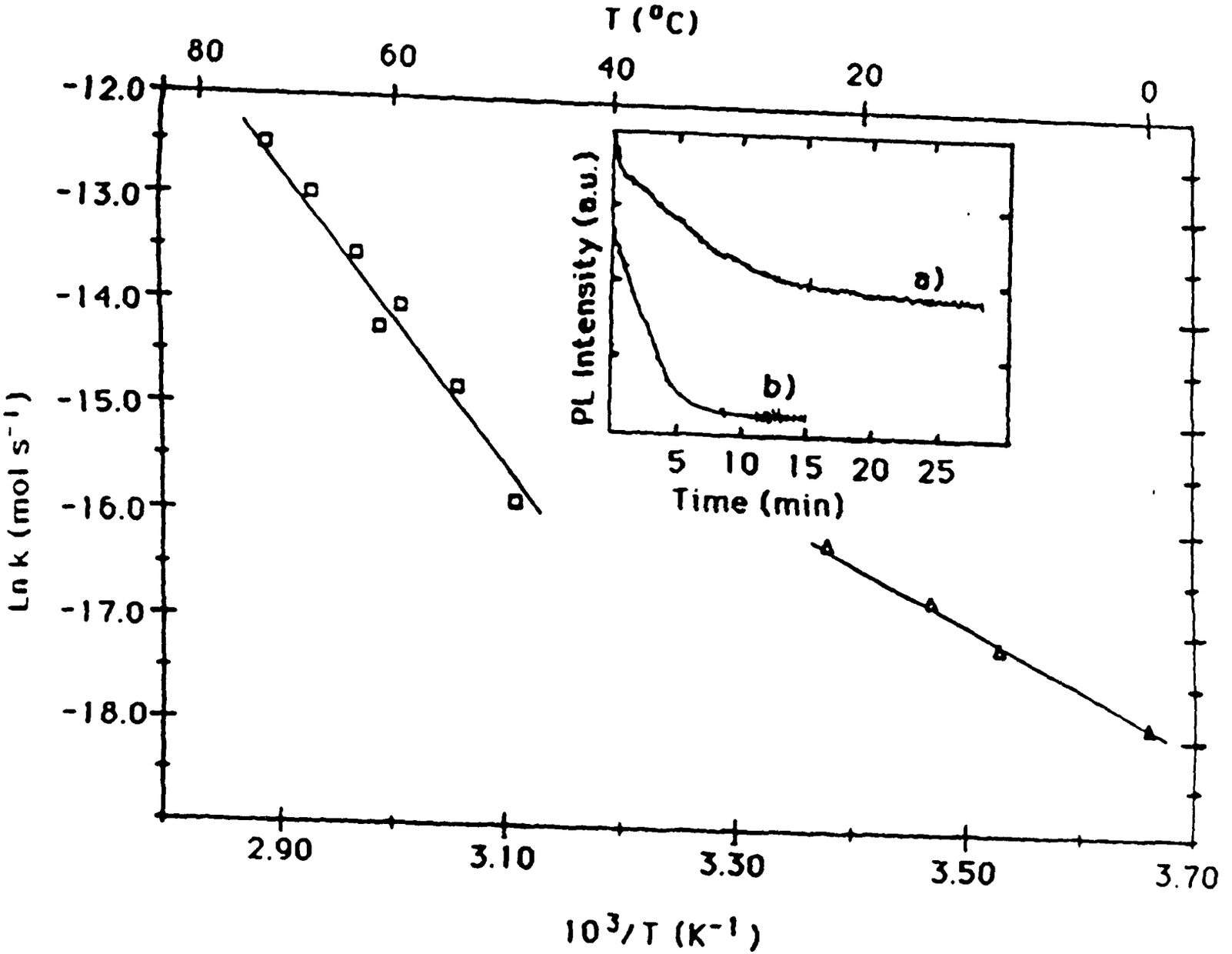
13. When the reaction is monitored by powder X-ray diffraction, it is found to proceed through an initial loss of crystallinity of HUP, accompanied by loss of PL intensity. Our results, which yield rates for the disappearance of HUP, do not permit us to say whether direct conversion of HUP to UP occurs, 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 $\sim 75^{\circ}C$, 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 Mets. **1985**, 108, 189. DSC traces of the octahydrate reveal a phase change at $110^{0}C$, 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.

Figure Caption

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 $\pm$0.5 $^0$C. Inset: Representative PL decay curves for HUP decomposition at a) 60$^o$C and b) 70$^o$C. The initial PL intensities have been offset for clarity.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40
20
0
-12.0
-13.0
-14.0
-15.0
-16.0
-17.0
-18.0
Ln k (mol s⁻¹)
2.90
3.10
3.30
3.50
3.70
10³/T (K⁻¹)
PL Intensity (a.u.)
a)
b)
5
10
15
20
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Time (min)

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