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Studies of Layered Uranium(VI) Compounds. II. Thermal Stability of Hydrogen Uranyl Phosphate and Arsenate Tetrahydrates

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By means of accurate TGA, we have shown that the proton-conducting solid electrolytes $HUO_2PO_4 \cdot 4H_2O$ (HUP) and $HUO_2AsO_4 \cdot 4H_2O$ (HUAs) are more correctly represented as $HUO_2P/AsO_4 \cdot (A\text{-}x)H_2O$, where A is assumed to be the integral number 4. The water deficiency x was estimated to be less than 0.03 at 295°K, but increased respectively by less than 0.1 and 0.05 when HUP and HUAs were heated in air to approximately 315°K. At higher temperatures, dehydration of HUP under isothermal conditions produced, over a temperature interval of less than 2°K, a lower hydrate phase having approximately 1.5 waters of crystallization. Equilibrium dehydration temperatures were established for HUP over a range of humidities, and varied from 297°K at 0.4 mm Hg water vapor pressure, to 318°K at 16 mm Hg pressure. An explanation of the apparently high standard molar enthalpy for dehydration is suggested in terms of small losses of a phosphorus-containing compound accompanying the water loss. The overall phase relationships of HUP are discussed.

Introduction

Our recent observation of high proton conductivity in hydrogen uranyl phosphate tetrhydrate, $HUO_2PO_4 \cdot 4H_2O$ (HUP) (*1, 2*) has prompted us to investigate the thermal stability of the hydrate under near-ambient conditions. Although there have been previous studies of the dehydration behavior of HUP (*3–8*) and HUAs (*3, 8*), the weight loss characteristics and the composition of the products appear to depend on conditions in a way which is not yet understood. For example, a review of the data on HUP would appear to indicate that the first dehydration product could either be the monohydrate (*3, 4*), the dihydrate (*7*), or possibly intermediate compositions (*8*). Several factors are known which may complicate the thermogravimetric behavior. First, Kobets *et al.* have shown (*5, 7*) that a phosphorus-containing compound is lost to the gas phase in small amounts before all the water is lost. Second, the condensation of the phosphate groups to polyphosphates, such as $P_2O_7^{4-}$, with the liberation of water from the structure, has been shown to occur at temperatures as low as 423°K (*5*). This process proceeds, and is eventually accompanied by loss of oxygen, to give a compound close in composition to the reduced uranium (V) oxide pyrophosphate $U_2O_3P_2O_7$ at 1170 to 1270°K (*9, 10*).

The properties of HUP and its analogs are of particular interest since so few other layered hydrates are known. Among these are the classes represented by $CaSO_4 \cdot 2H_2O$ (*11*), $SnCl_2 \cdot 2H_2O$ (*12*), $Cu(HCOO)_2 \cdot 4H_2O$ (*13*), $K_4Fe(CN)_6 \cdot 3H_2O$ (*14*), and the hydrated clays (*15*). Within this group, the

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structures of HUP and HUAs resemble most closely that of the clays. Negatively charged layers of $(UO_2P/AsO_4)_n^{n-}$ are interspaced by staggered layers of water molecules and counterbalancing cations (*16*, *17*), which are H^+ in HUP, but may also be most other cations. Montmorillonite and vermiculite clays also possess negative layers. Of the layered hydrates, only the HUP class and the clays have water molecules which are not coordinated to cations in the layer framework. These hydrates might therefore be expected to show different dehydration behavior compared to the other layered hydrates.

We have studied HUP and HUAs, mainly in the temperature range 295 to 350°K, spanning the first transition, in order to clarify the origin of the weight losses observed. A controlled water vapor system was used, in conjunction with a sensitive thermogravimetric analysis (TGA) instrument, so as to cover atmospheric conditions such as may be encountered in the use of electrochemical cells containing HUP as the solid electrolyte (*18*). Equilibrium data were obtained, where necessary, under isothermal conditions. Small weight losses detected before the onset of the major dehydration were checked using single-crystal samples so as to indicate any effects of particle size or dislocations.

Experimental

HUP was prepared in the same manner used previously (*2*), by mixing a solution containing 25 g AR uranyl nitrate dissolved in 20 ml distilled water with 22 ml 2.3 *M* AR phosphoric acid at room temperature. The precipitate, which slowly formed, was filtered and washed with phosphoric acid solution of pH 2 until the equilibrium wash solution was between pH 1 and 2, and allowed to dry in air to produce $HUO_2PO_4 \cdot 4H_2O$, as previously confirmed by analysis (*2*). HUP is known to exist in three slightly different structural forms (*19*), as previously discussed (*2*). X-Ray data showed that type I was produced by the above preparation, and similar preparations using more dilute solutions. The previous substantial TGA studies of Kobets *et al.* (*4–7*) and Weigel and Hoffmann (*8*) have also almost certainly been done on the type I form, as inferred from the preparative conditions for the former and the lattice dimensions for the latter.

HUAs was prepared in a manner similar to that used for HUP, and was characterized by chemical analysis, TGA, and X-ray spectroscopy. The lattice parameters, which will be discussed in detail in Part III, were in general agreement with those given in previous TGA reports for HUAs (*3*, *8*). Single-crystal platelets of HUP and HUAs, about 1 mm wide, were grown from concentrated solutions by slowly lowering the temperature. The crystals were washed with pH 2 acid and dried in air prior to the TGA runs.

TGA results were obtained using a Stanton–Redcroft TG-770 thermogravimetric microbalance having the batteries replaced by a stable dc supply. Thermal insulation was placed around the microbalance section, to improve the long-term stability to give daily drifts of typically less than 5 μg. Short-term stability was better than 1 μg. A special slow ramp gave heating rates down to 0.08°K min^{-1}.

For runs of the highest accuracy, laboratory air was made to flow over the sample at a rate of between 2 and 30 ml min^{-1}. Other runs were done, primarily aimed at establishing the decomposition temperatures, using a water vapor–nitrogen flow, at 30 ml min^{-1}, over the sample in the opposite direction in order to reduce the time lag after a humidity change. The balance was recalibrated for each condition. The water vapor pressures were established by mixing dry nitrogen with nitrogen saturated with water vapor at 297.8°K, using calibrated *in situ* flowmeters. The calculated value at 0.4 mm

Hg (0.05 kN m^{-2}) agreed with that obtained gravimetrically using three U-tubes filled with finely ground silica gel, which had been preheated to 420°K and which is a suitable absorbent for the flow rates and pressures used (*20*).

Results

TGA results for HUP in air using heating rates of 5°K min^{-1} were very similar to those previously reported using a similar flow system (*3–5*). Most of the water was lost between about 330 and 340°K to give a weight corresponding to approximately a 1.5-water form. At higher temperatures the weight decreased gradually, by an amount equivalent to 1 to 1.5 waters per formula at about 490°K, and more slowly but continually right up to 1270°K to form what is probably $U_2O_3P_2O_7$.

In contrast to such an apparently broad initial transition, isothermal measurements showed the transition to be in fact very sharp. Typical results are shown in Fig. 1 for a range of water vapor pressures. The entire weight loss corresponding to the transition occurred within 2°K for each sample. The rates of losses were very slow and dehydration took typically 10 hr to complete. Calculations showed that the water loss was limited by the rate of its removal by the gas stream, which was flowing at 30 ml min^{-1}. If the weight loss is expressed in terms of numbers of water molecules lost per formula, the results show a loss of between 2.5 and 2.6 waters. The points above the transition were typically obtained after 2 hr at each temperature, after which the weight changes had reached plateaus, as further established by waiting for up to 16 hr for a few points. The continued weight losses above the transition temperatures, as can be seen in Fig. 1, are therefore not the consequence of obvious time effects.

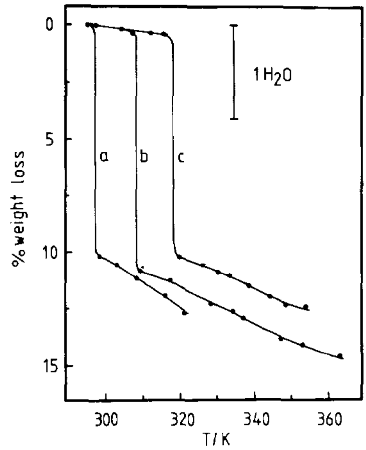

FIG. 1. Thermograms of HUP powder (approximately 10-mg samples). Solid circles represent equilibrium weights obtained at constant temperatures. The weight change expected from the loss of one water molecule per formula is indicated. The increase in transition temperatures from 297 ± 1 to 308 ± 1 to 318 ± 1°K with increasing water vapor pressure from 0.4 to 3.0 to 16 mm Hg (0.05, 0.40, and 2.1 kN m^{-2}) is clearly evident. The vapor pressures were determined to an accuracy of ±10%.

When samples were continually heated at normal TGA rates up to 5°K min^{-1}, it was found that the initial indication of a weight loss occurred at the same temperature as that obtained isothermally, but that the remaining weight loss was spread over a larger temperature range, the effect being accentuated at higher heating rates. Since the transition temperature is pressure dependent, rapid liberation of water into the gas stream will increase the vapor pressure over the sample and suppress further weight losses.

A run was done using oxygen-free nitrogen directly, to give a much lower water vapor pressure, and the sample was just held at the room temperature of 296°K. Weight loss began immediately and the eventual weight loss corresponded to 3.0 water molecules per formula, which was significantly different from the values of 2.5 to 2.6 found at higher water vapor pressures.

It can be seen from Fig. 1 that even for the data taken under equilibrium conditions there is a small weight loss prior to the main transition. We have investigated this region in more detail using both powders and batches of single crystals. Figure 2 shows a typical temperature-stepped thermogram for HUP single crystals, confirming a small weight loss, corresponding to about 0.1 water per formula, before the main transition. The sample weight was constant to within 0.02% during 3 days prior to the run. The small amounts of water liberated during the run were insufficient to significantly alter the water vapor content of the purge gas, and the rate of attainment of the equilibrium weights was therefore quite rapid.

The cooling portion of the thermogram shown in Fig. 2 reveals two types of processes. Most of the weight lost during heating is rapidly regained when the temperature is returned to the initial value. However there is an experimentally significant overall weight loss, labeled w_i in Fig. 2, which did not alter by more than 0.015% of the total weight over the next day, and is therefore irreversible over this time period. Such behavior was typical of all the powders and single crystals of HUP and HUAs investigated, although the irreversible component was barely significant in the case of the HUA samples.

The weight changes observed during heating HUP single crystals and powders, and HUA single crystals, are compared in Fig. 3, and are seen to be very comparable to each other. In particular, both HUP single crystals and powder lost a weight equivalent to about 0.1 water per formula over the 20°K interval. Similarly, both HUA single crystals and powder (data not shown) lost weights equivalent to about 0.05 water per formula over a 20°K interval. In the case of HUAs a small change in the weight was observed at the paraelectric–antiferroelectric transition, as can be seen at 301°K in Fig. 3.

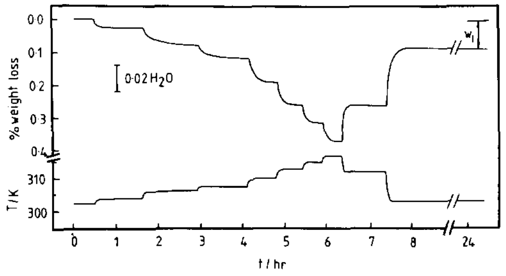

FIG. 2. Thermogram of a batch of HUP single crystals (14.5 mg) in the temperature region before the main transition, showing the small rapid and reversible weight changes, together with an underlying and predominantly irreversible weight loss (w_i). Atmospheric air was passed over the sample at 10 ml min^{-1}.

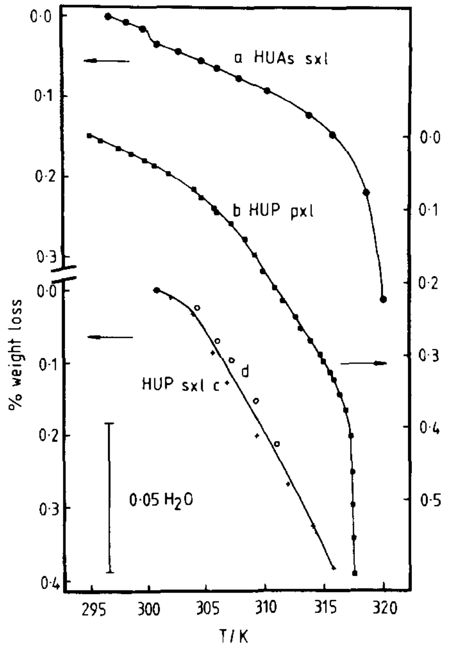

FIG. 3. Weight loss versus temperature in the nonstoichiometric region. The data for HUAs (4.251 mg) and HUP (14.51 mg) single crystals were obtained at isothermal points using an air flow of 10 ml min^{-1}. The data for HUP single crystals (c) represents the weights shown in Fig. 2. The data for HUP powder (b) (27.0 mg) was obtained during continuous heating at a rate of 0.08°K min^{-1} in an air flow of 3 ml min^{-1}.

Discussion

The results from the range of experiments performed on HUP have enabled us to establish the phase compositions and relationships for near-ambient conditions. It is clear that the phase transition from approximately the 4-water form to approximately the 1.5-water form is surprisingly sharp, occurring within a few degrees. This is typical of crystalline hydrates such as $CuSO_4 \cdot 5H_2O$ (*21*), but contrasts with the behavior of the clays (*15*), and would be consistent with rigid-like water lattices in HUP and HUAs compared to liquid-like water layers found in the clays (*15*).

Turning to the composition of the tetrahydrate phases of HUP and HUAs, we attribute the small weight changes which occur before the transition mainly to an equilibrium loss of water from the lattice to form a defect phase having water vacancies. This can be formulated as $HUO_2P/AsO_4 \cdot (A\text{-}x)H_2O$, where A is assumed to be the integral number 4, and where x typically extends from zero up to at least 0.1 for HUP and to at least 0.05 for HUAs before the phase transition begins. The possibility of the loss arising from surface water can be discounted on the basis that the powder, comprising of micrometer-sized crystallites, had a surface area approximately 1000 times that of the same weight of the large single crystals. Similarly, the equality of the powder and single crystal results is inconsistent with weight losses arising from a phase change to the lower hydrate occurring at imperfections at lower temperatures than the main transition.

The activation energy for the extent of nonstoichiometry should be similar to the molar enthalpy of dehydration, evaluated for transitions in HUP at higher temperatures to be about 60 kJ mol^{-1} (*7*). The data obtained for both single crystals and powders show that this is approximately the case, and that for all reasonable values of the enthalpy the vacancy concentration at 293°K is not greater than 0.03 water molecule per formula. Many analytical determinations of the water content in HUP have been made (*4, 8, 17*), and show a room-temperature composition having 4.0 ± 0.1 water molecules per formula, implying an integral value of 4 for A in the formula just mentioned. We have not evaluated the thermodynamic parameters for vacancy formation more precisely because of the likelihood of simultaneous loss of a phosphorus-containing compound, as discussed below.

Knowledge of the variation of the transition temperature with vapor pressure should enable the enthalpy ΔH^θ and entropy ΔS^θ for the phase change from the 4-x-water form to the subhydrate to be evaluated, using the relationship

$$2.303\, R \log K_p = \Delta S^\theta - \Delta H^\theta / T, \qquad (1)$$

where R is the gas constant and $K_p = (p_{H_2O})^n$, where n is the number of moles of water removed. By dividing the expression through by n one can show that a plot of $\log (p_{H_2O})$ versus $1/T$ will yield the entropy and enthalpy changes per mole of liberated water. Figure 4 shows such a plot of the data.

Also plotted for comparison are the equilibrium data of Kobets *et al.* (*7*), as read from

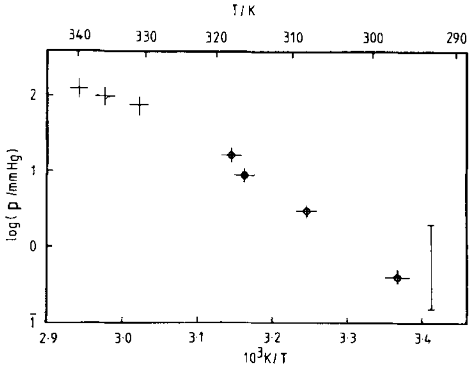

FIG. 4. Variation of $\log(p_{H_2O})$ with $1/T$ at the phase transition from the 4- to the approximately 1.5-water form of HUP (ringed crosses). The value at 316°K was obtained from curve *b* in Fig. 3. The remainder were obtained from the runs shown in Fig. 1. Also shown are data obtained at higher temperatures using closed systems for the change from the 4- to the approximately 2-water form (crosses (*7*) and solid circle (*8*)). The bar shows the data for the 4- to the 1-water transition (*4*).

the published pressure–temperature plot obtained using sealed systems. The equilibrium dehydration temperature of approximately 335°K at 92.5 mm Hg (12.3 kN m^{-2}) water vapor pressure, as obtained by Weigel and Hoffmann (*8*) using a static system, is also plotted and is in agreement with these results. In addition to the high-temperature values, Kobets *et al.* also obtained information at 293°K (*4*) by equilibration with concentrated sulfuric acid solutions in a closed container. The tetrahydrate was stable at 2.8 mm Hg (0.37 kN m^{-2}), but had transformed completely to give 1.0 water per formula, by analysis, at a pressure of 0.15 mm Hg (0.020 kN m^{-2}). These two limits are indicated in Fig. 4.

The four types of experiment represented in Fig. 4 cover different pressure ranges, and produce three different products, having respectively close to 2, 1.5, and 1.0 waters of hydration for high, intermediate, and lower temperatures. This order appears to be the reverse of the normal expectation of greater water loss at higher temperatures. The gradients given by the points, which normally represent the molar standard enthalpy change for water, might be expected to be similar for the three transitions. The values of ΔH^θ for the high-temperature set of data shown in Fig. 4, and for subsequent dehydrations at even higher temperatures, were found to be 52, 56, and 65 kJ mol^{-1} for the 4 to 2, 2 to 1.5, and 1.5 to 0 water transitions, respectively (*7*). These values are similar to those for evaporation of water or sublimation of ice. A value nearly three times as large, as suggested by the large gradient of our data points, would suggest the presence of additional factors.

Of the four types of experiment represented in Fig. 4, only our experiments were done in a flowing gas stream, the rest being performed in sealed systems. One factor which could therefore uniquely affect our results could be loss of a phosphorus-containing compound, such as P_2O_5 or H_3PO_4, at a rate faster than in the sealed systems. Kobets *et al.* (*7*) found 10^{-2} to 10^{-3}% P_2O_5 in solutions which had been heated in sealed two-compartment vessels with HUP over the temperature range 360 to 870°K. In another experiment (*5*), a white phosphorus-containing solid sublimed off at high temperature, and after a sample was maintained in a flow of moist air at 873°K for 6 hr 16% of the initial P in the HUP had been lost. This corresponds in weight to approximately 0.9 water in HUP. The phosphorus loss was found to be much less in a stream of dry gas.

If phosphorus loss, like condensation to give polyphosphates (*5*), were a continuous function of temperature from room temperature upward, it would not be unrealistic if the phosphorus losses were around the percent level at the temperatures of our experiments. Phosphorus loss, at about the 0.4% level, would in fact provide an explanation for the irreversible component, w_i, in Fig. 2, found from our thermal studies of the pretransition region.

Rough calculations show that phosphorus losses at the level of several percent could account for the apparently high ΔH^θ and ΔS^θ values indicated by our data. Both phosphorus and water losses will need to be included in these terms, and the individual contributions cannot be obtained without further data concerning phosphorus contents and vapor pressures of the gaseous component. The corresponding relationship to Eq. (1) may now be nonlinear for $\log p_{(H_2O)}$ vs $1/T$. The apparently high dehydration enthalpy can therefore satisfactorily be accounted for on the basis of loss of a phosphorus-containing compound. Such losses, which are fixed for given temperatures and vapor pressures of water and phosphorus-containing compounds, are probably governed by solid state defect equilibria, and do not reflect an inherent instability of HUP towards decomposition.

Phosphorus loss over long times may render the real water contents of the first dehydration product slightly higher than the figure of 1.4 to 1.5 previously indicated. Furthermore, the evidence of Kobets *et al.* (*5*, *7*) of polyphosphate formation, at temperatures as low as 363°K, with associated liberation of water, will add a further factor leading to water contents which cannot be exactly related to possible simple arrangements of water molecules within the water layer network.

Our results, combined with previous evidence, show that HUP, unlike the clays, behaves, in all but the final stages of dehydration, as a series of almost-fixed composition hydrate phases having approximately 4.0, 2, 1.5, and 1.0 water molecules per formula, although not produced in this order by heating. To explain this last fact we can postulate a phase diagram such that the 2-water form would disproportionate to the 4- and 1.5-water forms if cooled in a sealed system below about 330°K, and similarly that the 1.5-water form would disproportionate to the 4- and 1-water forms if cooled in a sealed system below about 295°K. The exact composition of these phases has been shown to be influenced by nonstoichiometry both in the water layers, and probably also in the uranyl phosphate layers, where water or OH^- may displace the phosphate groups and coordinate directly to the uranyl ions, liberating P_2O_5 or H_3PO_4 from the lattice. The results show that HUP is an essentially stable hydrate over all likely ambient conditions and at higher temperatures, depending on the humidity level. For example at about 6 mm Hg (0.8 kN m^{-2}) water vapor pressure (30% relative humidity at 293°K) HUP is stable up to 312°K.

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