Kinetics of Dehydration of Single Crystals of Uranyl Nitrate Hexahydrate

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The kinetics of dehydration of single crystals of uranyl nitrate hexahydrate to uranyl nitrate trihydrate have been followed isothermally, *in vacuo* from −60 to −30 °C. The energy of activation for the dehydration is 46 ± 4 kJ (mol H_2O)$^{-1}$. The dependence of the rate of dehydration upon the ambient water vapour pressure is linear which is unusual. Although the product is crystalline and this is a non-zeolitic dehydration process, it does not occur at the reactant–product interface and, consequently, the usual contracting envelope kinetics do not apply.

THERE have been several investigations of the dehydration of uranyl nitrate hexahydrate (UNH) by thermal analytical techniques [1-4] but detailed kinetic data have not been obtained by conventional isothermal techniques. Differential thermal analysis (d.t.a.) studies have shown [3] that UNH dehydrates stepwise in nitrogen as follows:

$$\text{UNH} \longrightarrow \text{UNT (59 °C)}, \Delta H = 52{\cdot}3 \text{ kJ (mol } H_2O)^{-1}$$
$$\text{UNT} \longrightarrow \text{UND (72 °C)}, \Delta H = 55{\cdot}6 \text{ kJ (mol } H_2O)^{-1}$$
$$\text{UND} \longrightarrow \text{UNM (141 °C)}, \Delta H = 75{\cdot}7 \text{ kJ (mol } H_2O)^{-1}$$
$$\text{UNM} \longrightarrow \text{UN (176 °C)}, \Delta H = 68{\cdot}2 \text{ kJ (mol } H_2O)^{-1}$$

where UND, UNM, and UN refer to the dihydrate, monohydrate, and anhydride, respectively. Smith [3] noted that all of the lower hydrates and the anhydride exhibit X-ray powder patterns in agreement with those reported in the literature.[4]

Thermodynamic values for the formation of the various uranyl nitrate hydrates are available in the literature; [5] these allow the equilibrium vapour pressures over the various pairs of hydrates to be determined. Direct measurements of the vapour pressures have been made.[4,6] The most recent values [6] do not agree with those calculated from the thermodynamic data for formation of these hydrates; [5] the latter appear to be in error because they predict an equilibrium water vapour pressure for UNH–UNT greater than that of liquid water.

Taylor and Mueller [7] have determined the structure of UNH by neutron diffraction. They found that the uranyl group is surrounded equatorially by a near-planar oxygen hexagon of four oxygen atoms from two non-equivalent bidentate nitrate groups and two oxygen atoms from equivalent water molecules. In addition to the co-ordinated water molecules, there are four moles of structural water which are hydrogen-bonded to the nitrate ion oxygens and to each other. The water molecules lie in sheets perpendicular to the *a* axis (Figure 1). An inelastic neutron scattering study of

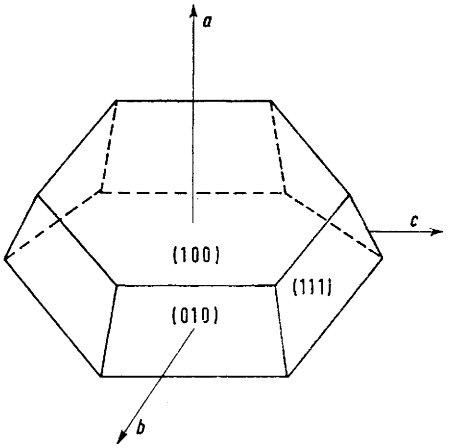

FIGURE 1 Typical crystal habit of UNH employed for these studies

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[1] J. K. Dawson, *J. Chem. Soc.*, 1956, 3533.

[2] W. Lodding and L. Ojamaa, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1261.

[3] W. H. Smith, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1761.

[4] A. J. King, R. Pfeiffer, and W. Zeek, USAEC Report, 1957, N.Y.O. 6313.

[5] W. Latimer, 'Oxidation Potentials,' Prentice-Hall, New York, 1952.

[6] V. M. Vdovenko and A. P. Sokolov, *Radiokhimiya*, 1959, **1**, 117.

[7] J. C. Taylor and M. H. Mueller, *Acta Cryst.*, 1965, **19**, 536.

UNH by Rush *et al.*[8] showed that the hydrogen-bonding of the structural water molecules to the nitrate oxygen is weak. The thermal motion of the co-ordinated water molecules is less than that of the structural water molecules.[7]

The structure of UNT has been determined by X-ray diffraction by Vdovenko *et al.*[9] They report that the uranyl ion retains the co-ordination reported for the hexahydrate; the third water molecule is outside this co-ordination sphere and is hydrogen-bonded to one of the nitrate ions.

The structure of UND has also been determined by X-ray diffraction by Vdovenko *et al.*[10] and more recently by neutron diffraction by Dalley, Mueller, and Simonsen.[11] Details of the structures given by these groups were not in accord but both did show that the uranyl group is co-ordinated to a hexagon of oxygen atoms derived from the nitrate ions and water molecules.

The self-diffusion of water in UNH was recently examined by the authors,[12] and it was found that the four moles of structural water undergo exchange with D_2O or $H_2{}^{18}O$ but the co-ordinated water does not ($\leqslant$35 °C). The self-diffusion of water in single crystals of UNH is easier than in other hydrates which were examined. It is of interest to determine whether this high mobility affects the kinetics of dehydration.

EXPERIMENTAL

Single crystals of UNH were prepared by the method of Taylor and Mueller.[7] Individual single crystals of *ca.* 1 mm^3 were used for dehydration. The kinetics of dehydration were followed gravimetrically *in vacuo*, *i.e.* the water vapour was continually removed during the dehydration process. The weight loss was followed either with quartz helix balances or with a type RG Cahn recording balance. For runs in the presence of water vapour thoroughly degassed water was deposited on glass wool which was maintained at a given temperature during a kinetic run. A Pirani gauge calibrated for water vapour confirmed the constancy of the pressure.

RESULTS

Single crystals of UNH, which were carefully handled in order to avoid artificial nucleation, dehydrated very rapidly *in vacuo* at room temperature so that detailed kinetic data had to be obtained below 0 °C. A typical dehydration curve is shown in Figure 2 (−19 °C, *in vacuo*). The fraction dehydration $\alpha_{6\rightarrow2}$ is defined on the basis of the loss of four moles of water as indicated in the subscript. Three features of interest emerge from this representative curve: (1) there is no induction period, (2) there is an extensive linear region, and (3) the change in slope corresponding to $\alpha_{6\rightarrow3} = 1$. Induction periods are usually noted in the dehydration of un-nucleated hydrate single crystals.[13] Since contracting envelope kinetics with dimensionality greater than one are generally observed for the dehydration of crystalline hydrates,[13] the extensive linear dehydration rate is unexpected. The change of slope indicates that the fourth mole of water is lost at a different rate than the first three. Smith [3] has observed endotherms in his d.t.a. results corresponding to these two processes, *i.e.* the first three moles of water were evolved at 59 °C and the fourth at 72 °C. This is noteworthy because these four moles of water appear to be bonded similarly within the lattice; [7] specifically, the four moles of water are composed of two pairs, each pair being structurally equivalent. At temperatures below −19 °C *in vacuo*, the fourth mole of water was not lost during the duration of the dehydration run. At room temperature in the laboratory atmosphere (where the dehydration is slow) the fourth mole of water was never lost.

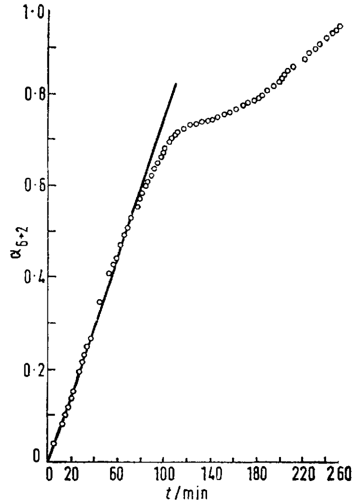

FIGURE 2 The dehydration of a UNH single crystal *in vacuo* at −19 °C

Before the determination of the energy of activation for the dehydration of crystalline hydrates, it is necessary to examine the dependence of the rate of dehydration upon the surrounding water vapour pressure,[13,14] in order to assess the role of water vapour upon the dehydration. This dependence was examined at −30 °C using individual single crystals of UNH; at this temperature the rate of dehydration was relatively low so that self-cooling should be small even *in vacuo*. The rate constant was determined from the slope of the linear region of the $\alpha_{6\rightarrow3}$ *versus* time plots. In the presence of water vapour the dehydration curves had the same shape as in its absence except that a small induction period appeared. The rate of dehydration declines linearly with water vapour pressure (Figure 3). This behaviour is unusual as shown by comparison with data for copper formate tetrahydrate [15] and potassium alum.[16] (The non-linearity of the data for potassium alum

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[8] J. J. Rush, J. R. Ferraro, and A. Walker, *Inorg. Chem.*, 1967, **6**, 346.

[9] V. M. Vdovenko, E. V. Stroganov, A. P. Sokolov, and G. Lungu, *Radiokhimiya*, 1962, **4**, 59.

[10] V. M. Vdovenko, E. V. Stroganov, and A. P. Sokolov, *Radiokhimiya*, 1963, **5**, 97.

[11] N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1971, **10**, 323.

[12] M. Franklin and T. B. Flanagan, *J. Phys. Chem.*, 1971, **75**, 1272.

[13] W. E. Garner, ' Chemistry of the Solid State,' Butterworths, London, 1955.

[14] M. Smith and B. Topley, *Proc. Roy. Soc.*, 1934, **134***A*, 224.

[15] P. Fichte and T. B. Flanagan, *Trans. Faraday Soc.*, 1971, **67**, 1467.

[16] G. Acock, W. Garner, J. Milstead, and H. Willavoys, *Proc. Roy. Soc.*, 1946, **189***A*, 508.

can be more readily seen in ref. 16 where the data are presented on an expanded pressure scale.) From Figure 3 it can be surmised that for the determination of the energy of activation '*in vacuo*' the pressure cannot exceed $1{\cdot}33 \times 10^{-4}$ kN m^{-2} (10^{-3} Torr) (at −30 °C) otherwise inhibition will result. During typical runs at −30 °C it was noted that the pressure did not exceed this value, and it is concluded that at −30 °C or below inhibition caused by the evolution of water vapour from UNH is not an experimental problem.

The other major experimental difficulty encountered in dehydration reactions is self-cooling.[13,14] In a recent investigation of the dehydration of copper formate tetrahydrate self-cooling was examined.[15] Since the heats of dehydration, per mole of water, of UNH and copper formate tetrahydrate are comparable, the degree of self-cooling encountered should be similar at the same absolute rates of dehydration for crystals of similar size. At −10 °C, where self-cooling was shown to be insignificant for copper formate tetrahydrate,[15] its absolute rate of dehydration was comparable to that of UNH at −30 °C for crystals of similar size. Therefore, at temperatures ⩽ −30 °C self-cooling should not be an experimental difficulty for runs performed '*in vacuo*'.

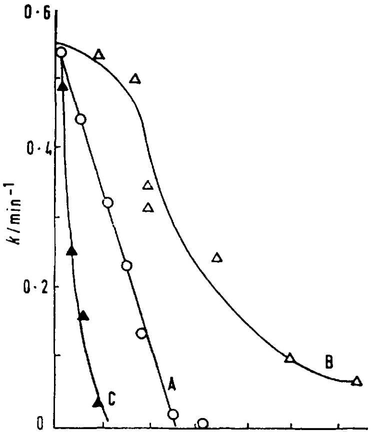

FIGURE 3 The effect of surrounding water vapour, expressed as vapour pressure relative to pure water, on the rate of dehydration of UNH compared to copper formate tetrahydrate and potassium alum. The rates have been normalized to that of UNH at $p = 0$. A, UNH at −30 °C, B, copper formate tetrahydrate 0 °C, and C, potassium alum at 30 °C

The energy of activation was determined from the slopes of the $\alpha_{6\rightarrow3}$ *versus* t plots over the temperature range −60 to −30 °C. This is the lowest range of temperature over which the dehydration kinetics of a crystalline hydrate have been heretofore examined and it illustrates the loosely bound nature of the structural water molecules in UNH. The Arrhenius plot is shown in Figure 4 and the slope gives $\Delta H = 46 \pm 4$ kJ (mol H_2O)$^{-1}$. Individual single crystals of comparable size, morphology, and weight (*ca.* 6 mg) were employed.

Dehydration runs were performed with individual single crystals whose faces had been selectively coated with water-impermeable plastic resin (Figure 5). It has been previously noted that this is a useful technique for demonstrating anisotropy in the dehydration process.[15] The rates of both runs shown (Figure 5) are slower than for an uncoated crystal of similar size. There is no marked difference, however, in the rates of dehydration of the top- and bottom- ({100} faces) coated and the side- ({010} and {111} faces) coated crystals. The surface area of the {100} faces and the combined {010} and {111} faces are approximately the same in the crystals employed. The rate of dehydration is thus proportional to the free surface area (uncoated) and macroscopic manifestations of anisotropy are absent in the dehydration. This is unexpected in view of the fact that the water molecules lie in infinite sheets parallel to the (100) planes.[7] In manganese(II) formate dihydrate[17–21] and copper formate tetrahydrate[15] a complete suppression of interfacial growth in one dimension occurs, *i.e.* the dimension perpendicular to the sheets containing the water

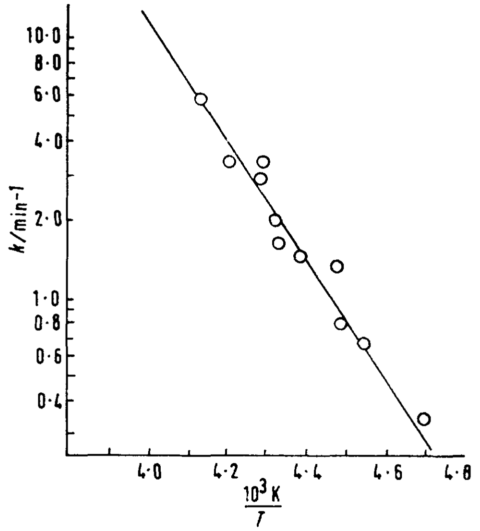

FIGURE 4 Arrhenius plot for the dehydration of single crystals of UNH from −60 to −30 °C *in vacuo*. Rate constant is expressed as $d\alpha/dt$ with t in min

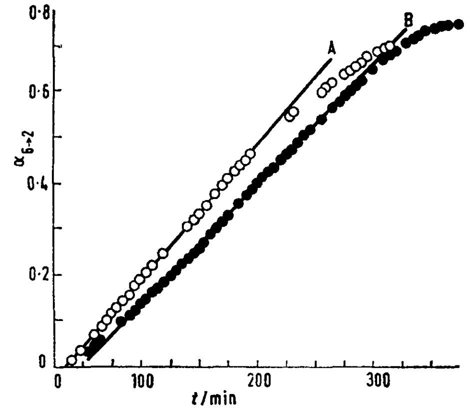

FIGURE 5 Dehydration of UNH single crystals coated with water impermeable resin on various faces (−19 °C, *in vacuo*). A, {100} faces coated; B, {010} and {111} faces coated

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[17] R. C. Eckhardt and T. B. Flanagan, *Trans. Faraday Soc.*, 1964, **60**, 1289.

[18] J. Thomas and T. Clarke, *J. Chem. Soc.*, 1968, 457.

[19] T. Clarke and J. Thomas, *Nature*, 1968, **219**, 1149.

[20] T. Clarke and J. Thomas, *J. Chem. Soc.* (*A*), 1969, 2227.

[21] T. Clarke and J. Thomas, *J. Chem. Soc.* (*A*), 1969, 2230.

molecules. It can be noted from Figure 5 that dehydration appears to cease at a stoicheiometry corresponding to UNT for the coated crystals but proceeds to the dihydrate for the uncoated sample.

Microscopic Observations.—Microscopic observations of the dehydration process were difficult because of the extreme fragility of the crystals. General features of interest emerged, however, from these observations which indicate that this is an unusual dehydration reaction.

The crystal faces all nucleate rapidly *in vacuo*. In the laboratory atmosphere nucleation occurs first on the {100} and {010} faces and somewhat later on the {111} faces. Many experiments were performed in which single crystals of UNH were allowed to dehydrate to a given value of α and were then cleaved. The cleavage planes were normal to the (010) and, surprisingly, the (100) planes. A typical cleavage experiment revealed that after $\alpha_{6\rightarrow3}$ attained a value of 0·65 the interface had penetrated only a small distance into the crystal. This suggests that the interface does not accurately reflect the extent of dehydration. For example, after $\alpha_{6\rightarrow3} = 0{\cdot}58$, an opaque region adjacent to the interface had dehydrated to only $\alpha_{6\rightarrow3} = 0{\cdot}7$ and a clear region adjacent to the interface had also dehydrated to a measurable extent, *i.e.* $\alpha_{6\rightarrow3} = 0{\cdot}22$. This convincingly demonstrates that the dehydration of UNH is not the usual interfacial process associated with the dehydration of crystalline hydrates.[13]

Rehydration.—A UNH single crystal was dehydrated at 0 °C *in vacuo* to UND. The latter was then rehydrated under varying water vapour pressures at 20 °C (Figure 6).

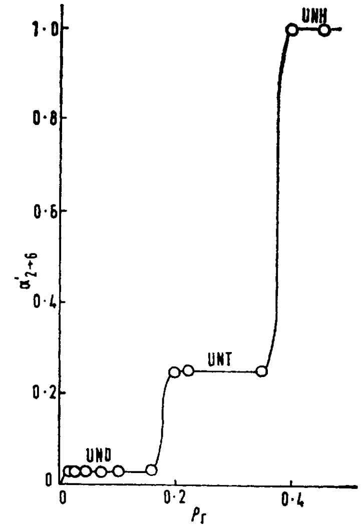

FIGURE 6 The equilibrium fraction of rehydration observed when UND is exposed to various relative water vapour pressures (20 °C)

Rehydration to UNT occurs in the range of relative (to liquid water) water vapour pressures, p_r, between 0·2 and 0·35. The supersaturation ratio required is, therefore, approximately 3 relative to the vapour pressure of the UNT–UNH system.[6] At a value of p_r in the range $0{\cdot}35 < p_r < 0{\cdot}40$ UNH first forms. Here the supersaturation ratio is very small. If the starting material is UND, UNH forms with no change of slope at the composition corresponding to UNT ($p_r > 0{\cdot}35$). In all cases the rehydration behaviour can be described by a dependence of α', where α' is the fraction of rehydration relative to the hydrate being formed, upon $t^{\frac{1}{2}}$ (Figure 7). This suggests that the slow step is solid-state diffusion.

X-Ray powder patterns were taken for virgin UNH, dehydrated UNH which was then rehydrated again to UNH, UNT, and UND. The *X*-ray patterns of the virgin UNH and the rehydrated UNH were identical to those given in the literature.[22] The patterns of UNT and UND exhibited broad, diffuse lines different from UNH. The invariant pressure over the UNT–UNH system attests to the fact that this dehydration process is not zeolitic, *i.e.* the product UNT is a distinct crystalline phase.

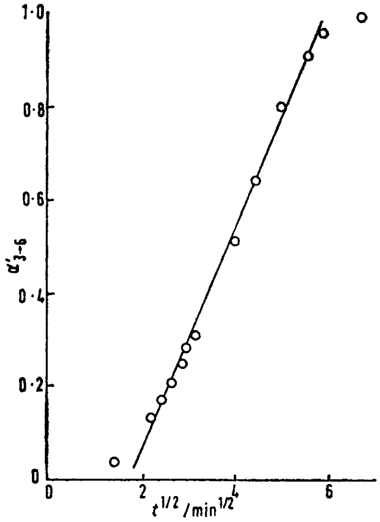

FIGURE 7 Kinetics of rehydration expressed as diffusion-controlled process for UNT ⟶ UNH (20 °C, $p_r = 0{\cdot}46$)

DISCUSSION

The solid-state dehydration of UNH reveals several unusual features which can be traced to the fact that the reactant–product interface is not the seat of reaction. Young [23] has suggested that such solid-state decompositions may exist but hitherto none have been reported.

The fact that the dehydration data do not follow a $t^{\frac{1}{2}}$ dependence indicates that solid-state diffusion is not the slow step; it can be shown that the presence of the reactant–product interface does not alter this conclusion.[24] Diffusion of water molecules through the UNH lattice *via* water vacancies must occur rapidly. An unusually large self-diffusion coefficient has been observed for water in UNH,[12] *e.g.* $D = 1{\cdot}8 \times 10^{-9}\ \mathrm{cm^2\,s^{-1}}$ (-19 °C), under static conditions which obtain in the presence of a constant rather large external water vapour pressure. The fraction of vacancies amongst the structural water in UNH under these conditions can be estimated at 8×10^{-7}.[12] The diffusion constant for these vacancies, in contrast to the diffusion constant for

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[22] J. D. Hanawalt, H. Rinn, and L. Frevel, *Ind. and Eng. Chem., Analyt.*, 1938, **10**, 457.

[23] D. A. Young, 'Decomposition of Solids,' 1966, Pergamon Press, Oxford.

[24] J. Crank, 'Mathematics of Diffusion,' 1956, Clarendon Press, Oxford.

the water molecules themselves, is therefore *ca.* $1 \cdot 5 \times 10^{-3}$ cm^2 s^{-1} (−19 °C). The rate of diffusion of vacancies within UNH is rapid enough to keep up with the observed rate of dehydration without the need for a large concentration gradient, *e.g.* the maximum concentration gradient of vacancies across the half-thickness of the crystal need be only 6×10^{17} vacancies cm^{-3}/cm during the early stages of dehydration (−19 °C). This is small compared to the concentration of *ca.* 10^{22} cm^{-3} noted in the clear portion of partially dehydrated UNH which was located adjacent to the interface. Therefore, UNH can sustain a large concentration of vacancies without recrystallization to the UNT lattice. These vacancies are highly mobile and nearly uniformly distributed during the dynamic conditions of dehydration. It is thus not unreasonable that diffusion is not the slow step. The observation that only a small penetration of the interface is noted when, for example, $\alpha_{6\rightarrow3} = 0 \cdot 67$ and yet the crystal becomes completely opaque at $\alpha_{6\rightarrow3}$ slightly less than one is explicable on the basis of these diffusion arguments. Diffusion through UNT occurs near the surface when $\alpha_{6\rightarrow3} = 0 \cdot 7$ and exclusively through this lattice when $\alpha_{6\rightarrow3}$ approaches one. Diffusion in the UNT lattice must also be rapid but measurements have not been made as yet.

Generally heterogeneous decomposition reactions occur at the reactant–product interface because the energy of activation is lowest there because of reactant–product co-operation.[23] If such an interfacial model were applicable to UNH ⟶ UNT, then it would be difficult to understand why *at the same temperature* UNT is formed and it subsequently dehydrates to UND (−19 °C, Figure 2). If all four moles of water can be removed at −19 °C, then it would be expected that all would be removed simultaneously in order to take advantage of reactant–product co-operation as the interface passes through the crystal.

The most probable explanation for the shape of the curve in Figure 3 is trivial; that is, it is due to the reverse reaction, rehydration. The net rate of dehydration must be equal to $R_0 - k_r p(\mathrm{H_2O})$, where R_0 is the rate at $p_{\mathrm{H_2O}} = 0$. Data for the equilibrium vapour pressure of the UNH–UNT system[6] are such that, within the limits of experimental error at $p = 1 \cdot 86 \times 10^{-3}$ kN m^{-2} (0·014 Torr) where the rate is seriously inhibited, p_{eq} could be as small as $3 \cdot 73 \times 10^{-3}$ kN m^{-2} (0·028 Torr). While the explanation of this inhibition is trivial, the fact that the reverse reaction can be observed under these conditions is not trivial because in other hydrate systems a specific inhibition is observed which occurs at vapour pressures considerably less than the equilibrium vapour pressures.[23] Dunning[25] has suggested that the inhibition of the rate of dehydration of crystalline hydrates can, in some cases, be described in terms of two-dimensional growth nucleation. The behaviour of UNH clearly cannot[25] and, therefore, two-dimensional nucleation is not a factor. Only a small supersaturation is required for rehydration of UNT to UNH, whereas most anhydrides or lower hydrates which have been examined require supersaturation ratios greater than one.[26,27] It is possible that most anhydrides or lower hydrates require two-dimensional nucleation for their rehydration too, whereas the UNT ⟶ UNH transformation does not. These questions will be deferred until a more detailed examination of the rehydration kinetics of single crystals of UNT is made.

In view of the absence of an induction period over the investigated temperature range, it is suggested that UNH readily forms highly mobile water vacancies *in vacuo via* evaporation of water molecules from the surface of the crystal. These vacancies are highly mobile and a defective UNH lattice is formed. There is an interface near the surface, but its role is unimportant in the dehydration process. Uranyl oxalate trihydrate dehydrates to form a pseudomorph of the original structure.[28] Young[23] has suggested that this is due to the aspherical nature of the uranyl ion and its co-ordinated oxalate ions. While the pseudomorph does relax here, the aspherical group about the uranium ion allows a large defect concentration to obtain. It is suggested that the slow step in the dehydration process is the desorption of water from the surface. The energy of activation is not inconsistent with this. The extensive linear region in the dehydration curve arises from this slow step. The rate is proportional to the concentration of water at the surface and is invariant from $\alpha = 0$ to 0·65. When the crystal turns opaque (this corresponds to the conversion to a defective UNT lattice) the rate declines.

This slow step accounts for the complete conversion to UNT and the subsequent conversion to UND ($\geqslant -19$ °C). Whenever a vacancy is formed with respect to the UNT lattice, it is eliminated by the migration of an interstitial water molecule into the vacancy. Thus UNT cannot begin to break down until the interstitial water is eliminated. Sufficient data are not available to allow a mechanism for the dehydration of UNT to be suggested. This would provide an interesting study because of its open lattice and the expected high mobility of water.

Despite anisotropy of the location of the water molecules within the lattice, anisotropy was not observed in the dehydration. The rate of dehydration was proportional to the uncoated surface area. This absence of anisotropy may be due to the nature of the slow step. It masks any manifestations of internal anisotropy.

The authors are grateful to the N.S.F. for financial support of this research and also to Dr. M. H. Mueller for a preprint of his paper on the structure of UND.

[1/1130 *Received, June 14th*, 1971]

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[25] W. J. Dunning, 'Kinetics of Reactions in Ionic Systems, Material Science Research,' vol. 4, eds., T. J. Gray and V. D. Frechette, Plenum Press, 1969.

[26] R. C. Eckhardt, P. Fichte, and T. B. Flanagan, *Trans. Faraday Soc.*, 1971, **67**, 1143.

[27] P. Fichte and T. B. Flanagan, to be published.

[28] A. Boullé, R. Jary, and M. Dominé-Bergès, *Compt. rend.*, 1950, **230**, 300.