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Pulsed NMR Study of Proton Motions in Uranium Trioxide Hydrates

M. T. WELLER* AND P. G. DICKENS

Inorganic Chemistry Laboratory, South Parks Road, Oxford, England

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Pure samples of $UO_2(OH)_2 \cdot H_2O$, β-$UO_2(OH)_2$, and "α-$UO_3 \cdot 0.85H_2O$" have been synthesized. Pulsed NMR data from a wide temperature range have been interpreted in terms of structural features and proton motions for all three materials. Two types of water molecule reorientation have been observed in $UO_2(OH)_2 \cdot H_2O$ and characterized in terms of activation energies and correlation times for the motions (Motion A: $T_c = 2.2 \pm 0.5 \times 10^{-15}$ sec, $E_A = 29.0 \pm 4$ kJ mole^{-1}; Motion B: $T_c = 4 \pm 0.5 \times 10^{-13}$ sec, $E_A = 31.2 \pm 4$ kJ mole^{-1}). © 1988 Academic Press, Inc.

Introduction

Compounds of the general formulae $MO_3 \cdot nH_2O$ (n = 0–2) are well known in, for example, the molybdenum ($MoO_3 \cdot nH_2O$, n = 1, 2), tungsten ($WO_3 \cdot nH_2O$, n = 0.33, 1, 2), and uranium systems ($UO_3 \cdot nH_2O$, n = 0.33, 0.5, 1, 2) (*1, 2*). In $MoO_3 \cdot 2H_2O$, two types of water molecules occur; half of the molecules are coordinated directly to the metal atom with the remainder as discrete hydrogen bonded molecules between the layers of the metal–oxygen framework. $MoO_3 \cdot 2H_2O$ may be dehydrated by heating at about 50°C to produce yellow $MoO_3 \cdot H_2O$, in which the interlayer molecules have been removed but the metal–oxygen framework remains intact. Similar behavior is assumed for the tungsten system though the structure of these materials is not known. $UO_3 \cdot 2H_2O$ is believed to consist of $UO_2(OH)_2$ layers between which isolated water molecules are situated. $UO_3 \cdot 2H_2O$ is easily dehydrated at 120°C, exhibiting similar behavior to $MoO_3 \cdot 2H_2O$, to produce α-$UO_2(OH)_2$. Pulse NMR measurements have been carried out on polycrystalline samples of the molybdenum compounds and it was shown that no translational motion of protons occurs in these compounds at ambient temperature. The relaxation time behavior over the temperature range studied was assigned to 180° flips of the H_2O molecules. Motional parameters, in $MoO_3 \cdot 2H_2O$, were obtained for the flipping of H_2O molecules attached to Mo atoms and for a separate process involving flipping of interlayer H_2O molecules.

The broad line NMR behavior of $UO_3 \cdot 2H_2O$ and α-$UO_3 \cdot H_2O$ has been investigated by Porte, Gutowsky, and Boggs (*3*). Their samples of $UO_3 \cdot 2H_2O$ were prepared by addition of amorphous U_2O_7 to boiling water and digestion of the suspension at 100°C for 15 min. The product was dried at 105°C for 3 hr. This method was repeated by us and was shown to yield $UO_3 \cdot 2H_2O$ of reasonable purity but rela-

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* Author for correspondence and present address: Dr. M. T. Weller, Department of Chemistry, The University, Southampton S09 5NH, United Kingdom.

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tively poor crystallinity with an additional product of this preparation being $UO_3 \cdot 0.8H_2O$. The second moment, calculated in their work from the absorption spectrum at 77 K, was interpreted by them as demonstrating that some of the protons in the crystal are not present in H_2O groups and the compound is better described as $U_2O_5(OH)_2 \cdot 3H_2O$. The β-$UO_3 \cdot H_2O$ described by Porte, Gutowsky, and Boggs in a second paper (*4*) is almost certainly not the compound normally known by this description. The statement that the unit cell dimensions differ from those of $UO_2 \cdot 2H_2O$ by less than 5% is mysterious. The broad line NMR data on this compound demonstrate that it is almost certainly a hydroxide, and is probably α-$UO_2(OH)_2$ or a mixture of the two monohydrates.

Synthesis and Characterization

$UO_3 \cdot 2H_2O$. $UO_3 \cdot 2H_2O$ was prepared by the method described by Hoekstra and Siegel (5), by precipitation from a solution of UO_2^{2+} through the addition of base. Precipitation over a period of several months at room temperature produced highly crystalline material, crystal dimensions 20 × 10 × 1 μm.

A Guinier powder X-ray diffraction photograph was recorded and 51 lines were measured. Debets and Loopstra (*7*) indexed all the lines they recorded for a sample of dihydrate, using a diffractometer, on an orthorhombic unit cell of dimensions a = 13.977, b = 16.696, c = 14.672 Å. The powder diffraction pattern for $UO_3 \cdot 2H_2O$ was refined on this unit cell reasonably satisfactorily. However, some very weak lines observed by Debets were not found and others were reindexed to give a better refinement. The final refinement with a = 13.994, b = 16.709, c = 14.651 Å had all lines indexed with $h + k = 2n$, indicating that the cell was C-centered (see Table I).

α-$UO_3 \cdot 0.85H_2O$. α-$UO_3 \cdot 0.85H_2O$ was prepared from uranyl nitrate via γ-UO_3,

TABLE I

POWDER X-RAY DATA FOR $UO_3 \cdot 2H_2O$

Intensity	d_{obs}	d_{calc}	$h\ k\ l$
w	8.725	8.656	1 1 1
vvs	7.364	7.325	0 0 2
w	6.067	6.050	1 1 2
w	5.062	5.037	2 2 1
wd	4.852	4.879	1 3 1
m	4.452	4.444	1 1 3
w	4.025	4.017	0 4 1
vvw	3.833	3.830	3 1 2
ms	3.670	3.663	0 0 4
vs	3.592	3.587	2 4 0
vvs	3.496	3.498	4 0 0
vvw	3.383	3.403	4 0 1
vvs	3.225	3.221	2 4 2
vvs	3.160	3.157	4 0 2
w	2.962	2.953	4 2 2
mw	2.892	2.891	2 4 3
w	2.833	2.826	1 1 5
mw	2.738	2.736	0 6 1
w	2.639	2.638	4 4 1
w	2.590	2.587	2 6 0
m	2.532	2.530	4 0 4
w	2.466	2.465	5 3 1
w	2.446	2.442	0 0 6
w	2.421	2.421	4 2 4
mw	2.309	2.305	2 0 6
w	2.268	2.266	3 3 5
w	2.205	2.204	5 1 4
m	2.155	2.155	4 6 1
vw	2.124	2.120	1 7 3
m	2.088	2.089	0 8 1
ms	2.037	2.036	6 4 0
m	2.018	2.018	2 4 6
m	2.009	2.009	0 8 2
s	1.961	1.962	6 4 0
w	1.921	1.920	0 8 3
w	1.899	1.897	3 1 7
wd	1.878	1.880	6 4 3
vwd	1.836	1.831	0 0 8
mw	1.793	1.793	4 8 0
mw	1.748	1.749	8 0 0
mw	1.742	1.742	4 8 2
w	1.726	1.726	1 3 8
m	1.701	1.701	8 0 2
w	1.683	1.683	4 8 3
w	1.669	1.668	5 1 7
w	1.658	1.658	3 5 7
mw	1.626	1.631	2 4 8
m	1.614	1.613	8 4 0
w	1.542	1.542	2 10 3

Note. Orthorhombic refined parameters: a = 13.994(8), b = 16.709(11), c = 14.651(9).

synthesized using the method described by Lister (*8*).

$\gamma\text{-UO}_3$ was converted to $\alpha\text{-UO}_3\cdot 0.85\text{H}_2\text{O}$ by boiling with water. About 10 g of $\gamma\text{-UO}_3$ was added to 100 ml of distilled water and the suspension refluxed for 18 hr. The product was bright yellow. A powder X-ray diffraction pattern showed a pure phase indexed on an identical cell to that employed by Dawson (*9*).

$\beta\text{-UO}_3\cdot\text{H}_2\text{O}$. Samples of $\beta\text{-UO}_3\cdot\text{H}_2\text{O}$ were prepared hydrothermally. A sample of $\gamma\text{-UO}_3$ was heated in excess water to 200°C and the temperature maintained for 4 days. Powder X-ray data of the product showed a pure phase.

Thermogravimetric Analysis

Samples were analyzed for water content thermogravimetrically. $\text{UO}_3\cdot 2\text{H}_2\text{O}$ loses *over* 1 mole of water over the range 100–150°C to produce $\text{UO}_3\cdot 0.85\text{H}_2\text{O}$. Both monohydrates lose water in the temperature range 300–500°C to yield UO_3 and the results of the analyses given in Table II.

The values found for $\text{UO}_3\cdot 2\text{H}_2\text{O}$ and $\beta\text{-UO}_3\cdot\text{H}_2\text{O}$ are in good agreement with those expected. However, the alpha monohydrate consistently analyzed as $\text{UO}_3\cdot 0.85\ \text{H}_2\text{O}$; decomposition of the dihydrate proceeds via a "monohydrate" of this composition. Other workers have found that the alpha monohydrate normally occurs with a stoichiometry $\text{UO}_3\cdot x\text{H}_2\text{O}$ with x in the range $0.80 < x < 0.90$ (*9*), though Taylor's sample used for power neutron diffraction prepared by cooling $\beta\text{-UO}_3\cdot\text{H}_2\text{O}$ was described as $\alpha\text{-UO}_3\cdot 1.00\text{H}_2\text{O}$ (*10*).

TABLE II
RESULTS OF THERMOGRAVIMETRIC ANALYSES

Expected	Found
$\text{UO}_3\cdot 2\text{H}_2\text{O}$	$\text{UO}_3\cdot 2.01 \pm 0.02\text{H}_2\text{O}$
$\beta\text{-UO}_3\cdot\text{H}_2\text{O}$	$\text{UO}_3\cdot 1.01 \pm 0.01\text{H}_2\text{O}$
$\alpha\text{-UO}_3\cdot\text{H}_2\text{O}$	$\text{UO}_3\cdot 0.852 \pm 0.008\text{H}_2\text{O}$

NMR Experimental Method

A Bruker SXP pulse spectrometer was used in conjunction with Data-lab data accumulation equipment for NMR measurements. Data were obtained at a frequency of 20 MHz.

T_2 was normally measured by a 90° pulse and observation of the free induction decay. For very short T_2 the zero time resolution method of Powles and Strange (*11*) was used to overcome the instrument dead time. For $T_1 < 1s$ the inversion recovery method, a $180\text{y} - \tau - 90\text{y}$ pulse sequence was used. Long T_1's were measured using a saturation technique. The spin lattice relaxation time in the rotation frame, $T_{1\rho}$, was measured using the method of Hartmann and Hahn (*12*). M_2 was measured in the rigid lattice region by fitting a Gaussian to the echo formed in the Powles and Strange method.

Results

Nuclear Magnetic Resonance

$\text{UO}_3\cdot 2\text{H}_2\text{O}$. The variation of the second moment with temperature demonstrated by $\text{UO}_3\cdot 2\text{H}_2\text{O}$ has been described by Porte *et al.* and is particularly complex. The low temperature, rigid-lattice, value of $19.9 \pm 0.8\ \text{G}^2$, typical for a system containing H_2O and OH groups, falls in three stages between 150 and 350 K to about $2.0\ \text{G}^2$. This behavior was interpreted in terms of rotation of the water molecules and two other undefined motions.

Approximately 1 g of $\text{UO}_3\cdot 2\text{H}_2\text{O}$ was placed in a 7-mm-diameter NMR tube. Relaxation times T_1, T_2, and $T_{1\rho}$ ($B_1 = 11.7$ G) were recorded in the temperature range 340–140 K at a frequency of 20 MHz. The temperature range was limited by the decomposition of the sample and the instrument's operation range. The recorded data are shown in Fig. 1. M_2 decreases with temperature; the values recorded in this work

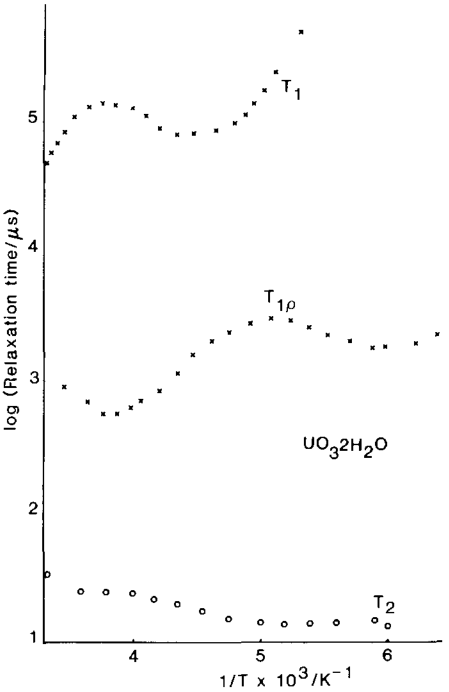

FIG. 1. Relaxation times T_1, T_2, and $T_{1\rho}$ as a function of inverse temperature for $UO_3 \cdot 2H_2O$.

are compared with those of Porte *et al.* in Fig. 2 and are found to be generally in good agreement though the plateau at approximately 12 G^2 is not visible. A low temperature second moment of 17.7 G^2 was determined from the curvature of the solid-echo at 140 K. This value probably increases slightly below this temperature and is in good agreement with the concomitance of H_2O and OH groups in the material.

The temperature dependent spin-lattice relaxation behavior shows that there is motion in this compound. The weak temperature dependence below approximately 200 K is typical of insulators at that temperature and results from relaxation via paramagnetic impurities giving a contribution $1/T_{\text{imp}}$ to the relaxation rate. T_2 increases only by a small factor (about 3) over the temperature range studied indicating that translation is not being detected. A likely explanation of the relaxation time behavior is 180° flips of water molecules about their C_2 axis, as has been observed in $MoO_3 \cdot 2H_2O$.

Two separate processes, A and B, are required to explain the spin-lattice relaxation behavior. As the temperature is raised above 150 K the decrease in T_1 is a result of Motion A and a minimum associated with this is discernible at about 225 K. Above 260 K T_1 again decreases, owing to Motion B, though the minimum associated with the motion presumably lies above the sample decomposition temperature. The observed T_1 is given by

$$1/T_1 = 1/T_{1A} + 1/T_{1B} + 1/T_1^{\text{imp}},$$

where T_{1A} and T_{1B} are the contributions from Motions A and B, respectively. The two measured $T_{1\rho}$ minima are associated with these motions. The T_1 and $T_{1\rho}$ data were analyzed assuming a BPP type dependence of T_{1A} and T_{1B} on τ_c, the correlation time. Activation energies for the two pro-

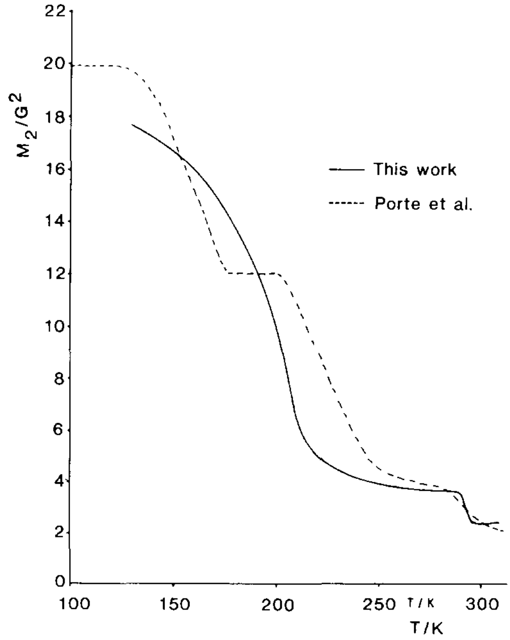

FIG. 2. Variation of second moment with temperature for $UO_3 \cdot 2H_2O$. The data of Porte *et al.* (3) are shown for comparison.

TABLE III
MOTIONAL PARAMETERS DETERMINED FOR $UO_3 \cdot 2H_2O$ AND OTHER HYDRATES

Compound	Data	τ_c (sec)	E_a (kJ mole^{-1})
$UO_3 \cdot 2H_2O$	T_{1A}	1.7×10^{-15}	29.0
	T_{1B}		31.2
	$T_{1\rho A}$	2.7×10^{-15}	
	$T_{1\rho B}$	4.0×10^{-13}	
$MoO_3 \cdot 2H_2O$	*A* (*13*)	6.5×10^{-16}	30.0
	B	2.0×10^{-15}	39.0
$CaSO_4 \cdot 2H_2O$	(*14*)	2.0×10^{-14}	26.0

cesses were determined from the gradient of the T_1 data on the low side of the minima, after correction for the effects of the paramagnetic centers. Correlation times were determined from the position of the T_1 and $T_{1\rho}$ minima (for Motion A). The values calculated τ_c, the preexponential factor, and E_a, the activation energies, are given in Table III.

The values for τ_c and E_a for Motion A are similar to those found for 180° flips of water molecules in other compounds (Table III), and the physical process affecting the T_1 data below 250 K is likely to be a similar motion. The loss of second moment of ≈ 16 G^2 between 140 and 250 K only partly supports this hypothesis. For a pure 180° flip of water molecules it has been shown that M_2^{intra}, the intramolecular portion, survives while M_2^{inter} is reduced. The expected decrease in second moment would thus be expected to be about 4 G^2 as is found for $MoO_3 \cdot 2H_2O$. The greater decoupling observed here indicates the motion must be more extensive and is probably a restricted rotational jump of the water molecule.

For Motion B τ_c is considerably larger than is normally observed for 180° water flips so the high temperature minimum is unlikely to be due to such processes in a second type of water molecule. In this temperature range M_2 drops to about 2.2 G^2; a similar value to this has been determined for α-$UO_3 \cdot 0.85H_2O$ at room temperature (see below) and is typical of a material containing discrete OH groups. A reasonable explanation of this behavior is a model in which the interlayer water molecules were rotating freely. The effect of this would be to remove M_2^{intra}, the major portion, leaving only a modified M_2^{inter} and the contribution from the isolated OH groups.

In summary, a reasonable model for the observed relaxation time behavior is as follows. Interlayer water molecules in $UO_2(OH)_2 \cdot H_2O$ are rigid below about 140 K. Above this temperature restricted rotation jumps occur removing part of the second moment. At even higher temperatures the H_2O molecules rotate freely about their oxygen positions reducing the second moment still further.

$UO_3 \cdot 0.85H_2O$. Pulsed NMR data for $UO_3 \cdot 0.8H_2O$ were recorded over a similar temperature range in order to see if the variations in relaxation times determined for $UO_3 \cdot 2H_2O$ could be associated with the discrete OH groups also present in the compound. T_1 data were collected in the range 200–540 K and are shown in Fig. 3. The very long T_1 values were recorded using a multiple pulse saturation sequence; for the longest T_1 recorded data collection times for each point were of the order of one hour. A value of T_2 at

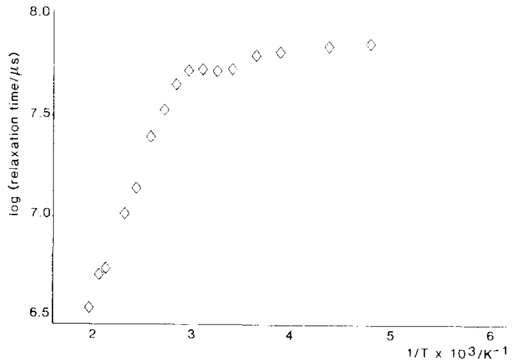

FIG. 3. Variation of T_1 for "α-$UO_2(OH)_2$" with inverse temperature.

200 K was deduced from a solid-echo of 28.2 μsec and M_2 at this temperature was determined to be 3.1 ± 0.1 G^2. This is in reasonably good agreement with the value determined by Porte *et al.* of 2.8 ± 0.1 G^2 and is typical of compounds containing discrete OH groups. T_1 for this compound is fairly constant below 350 K though above this temperature decreases quite rapidly. An activation energy for the process modulating T_1 of 34.5 ± 2 kJ mole^{-1} was determined after correction of the data for effects of T_1^{imp}.

It can be concluded that motions involving the hydroxyl proton in $UO_3 \cdot 2H_2O$ are unlikely to have an effect on the observed relaxation data as the highest temperature studied for this compound was 340 K.

It is of note that the monohydrate consistently analyses as $UO_3 \cdot 0.85H_2O$, which is certainly more correctly written $UO_2 \cdot (OH)_{1.7}O_{0.15}$ with a structure consisting of discrete uranyl groups bonded into a network by hydroxide and oxide ions. In such a network proton hopping between adjacent oxide ions is likely to occur as observed previously in materials such as $HTaO_3$ (*15*) and $HTaWO_6$ (*16*), where similar activation energies for this type of process are observed.

β-$UO_3 \cdot H_2O$. Samples of β-$UO_3 \cdot H_2O$ cooled to liquid nitrogen temperatures undergo a structural rearrangement to produce alpha monohydrate. For this reason samples of β-$UO_3 \cdot H_2O$ were not studied below room temperature. Measurements between room temperature and 500 K showed that T_1 was constant. The second moment determined at room temperature for this compound of 2.7 ± 0.4 G^2 is in good agreement with the experimental value given by Taylor (*10*) for this compound of 2.4 ± 0.3 G^2. The calculated value from the structure is 3.0 G^2.

In contrast of the alpha "monohydrate" no evidence of proton motion is observed which is consistent with the structure of β-$UO_3 \cdot H_2O$ (*10*). In this material, more correctly formulated $UO_2(OH)_2$ there is no vacant site to allow proton hopping.

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