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Thermal Dehydration and Structural Models of Two New Vanadyl Sulfate Hydrates

R. SCHNEIDER, J. R. GÜNTER,* AND H. R. OSWALD

Institute for Inorganic Chemistry, University of Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland

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The preparation of a new modification of vanadyl sulfate trihydrate, $VOSO_4 \cdot 3H_2O$, is described. In the course of its thermal dehydration, another new phase, $VOSO_4 \cdot 2H_2O$, is observed as an intermediate. Crystal data for the two compounds are: $VOSO_4 \cdot 3H_2O$, orthorhombic, $a = 8.980 \pm 0.006$, $b = 9.026 \pm 0.009$, $c = 7.776 \pm 0.003$ Å, space group $P2_12_12$; $VOSO_4 \cdot 2H_2O$, monoclinic, $a = 8.913 \pm 0.027$, $b = 8.93 \pm 0.09$, $c = 7.80 \pm 0.06$ Å, $\beta = 92.4 \pm 0.6°$. From the topotaxy of the dehydration reaction, structural models for the two phases are deduced. They consist essentially of $VOSO_4$ layers similar to those in α-$VOSO_4$ and interlayer water.

Introduction

A considerable number of hydrated and anhydrous phases of vanadyl sulfate, $VOSO_4 \cdot nH_2O$, have been described in the literature and characterized by their unit cell dimensions. For many, complete single-crystal structure determinations have been reported (Table I).

In the present paper, we describe the occurrence of two additional phases, not identical with any of those listed in Table I. Their thermal dehydration is studied, and from this and their crystal data, structural models are deduced.

Experimental

Preparation of Compounds

New form of $VOSO_4 \cdot 3H_2O$. This unknown compound was obtained by slight variation of the preparation procedure for monoclinic vanadyl sulfate trihydrate (the text in brackets refers to the unchanged procedure, as described in (*13*), producing the monoclinic form (*6, 7*)). 4.75 g of V_2O_5 was intimately mixed with 1.25 ml H_2O and 2.75 ml concentrated H_2SO_4 to form a thick paste, whereby considerable heat was developed. After 12–24 hr, 2.5 ml H_2O was added to the orange paste. In a water bath kept at 40°C, a stream of SO_2 was quickly (slowly) bubbled through the mixture, the product being so reduced until it became thick within 1–2 hr (reduction being stopped before thickening of the mixture, after about 45 min). The thickened, olive-colored paste was filtered (the thin olive mixture was filtered), leading to a deep blue filtrate. This was concentrated quickly in a boiling water bath (concentrated slowly during 1–2 days in a water bath held at 50°C). The resulting product was washed with little methanol and then with acetone, until it was acid free. The pale blue to pale

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* Author to whom correspondence should be addressed.

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TABLE I

LITERATURE DATA ON VANADYL SULFATE CRYSTAL STRUCTURES

Compound	Reference reporting existence of phase and crystal data	Reference for crystal structure determination	Remarks
$VOSO_4 \cdot 6H_2O$	(*1*)	(*2*)	Stable below 13.6°C
$VOSO_4 \cdot 5H_2O$(I)	(*3*)	(*3, 4*)	Stable form
$VOSO_4 \cdot 5H_2O$(II,β)	(*3*)	(*5*)	Metastable
$VOSO_4 \cdot 5H_2O$(III)	(*3*)	—	Metastable
$VOSO_4 \cdot 3H_2O$	(*6*)	(*7*)	
$VOSO_4 \cdot 2H_2O$(C)	(*8*)	—	Prepared by rehydration of $VOSO_4 \cdot \frac{3}{2} H_2O$
$VOSO_4 \cdot \frac{3}{2} H_2O$(B)	(*8*)	—	Prepared between 100 and 220°C
$VOSO_4 \cdot H_2O(\alpha)$	(*10*)	—	
$VOSO_4 \cdot H_2O$	(*9*)	—	
$VOSO_4 \cdot H_2O$(A)	(*8*)	—	Prepared under high water vapor pressure and high temperature
$VOSO_4$ (α)	(*10*)	(*12*)	
$VOSO_4$ (β)	(*11*)	(*11*)	

green product was dried in vacuum over P_2O_5. No indication of a take up of organic molecules from the washing media was observed. The new form of the trihydrate is not stable in air at room temperature, but quickly takes up water and deliquesces. It is, however, stable when kept under dry nitrogen.

$VOSO_4 \cdot 2H_2O$. This compound, not previously described in the literature in this modification, is obtained during thermal dehydration of the new modification of the trihydrate and is stable between approximately 180 and 230°C.

Characterization of Products

The products were characterized by means of X-ray diffraction on powders with a focusing Guinier IV camera (Nonius, Delft) and monochromatized Cu$K\alpha_1$ radiation, KCl being added as internal standard.

Continuous high-temperature X-ray diffraction patterns were recorded by means of a Guinier–Lenné camera (Nonius, Delft) under dry nitrogen and a focusing Huber camera system 600 in air with Cu$K\alpha$ and monochromatized Cu$K\alpha_1$ radiation, respectively, applying both linear and stepwise heating programs.

X-Ray diffraction line intensities were measured with a Joyce–Loebl double-beam microdensitometer.

Thermal decomposition was followed gravimetrically on a Mettler Thermoanalyzer TA-1 and on a Perkin–Elmer thermobalance TGS-2 in a flow of dry nitrogen or of dry synthetic air.

Morphological investigations and selected area electron diffraction were performed in a transmission electron microscope Hitachi HU-125 S.

Results

Orthorhombic $VOSO_4 \cdot 3H_2O$

The material prepared by the modified procedure described in the previous paragraph yields a powder X-ray diffraction pattern (Table II) not identical with any of the

TABLE II

POWDER X-RAY DIFFRACTION PATTERN OF ORTHORHOMBIC $VOSO_4 \cdot 3H_2O$

d_{obs} (Å)	d_{calc} (Å)	I/I_0 (%)	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I/I_0 (%)	*hkl*
7.7553	7.7760	68	001	1.9454	1.9461	12	421
5.8817	5.8912	74	011		1.9442		402
	5.8784		101		1.9440		004
4.4801	4.4900	16	200	1.7908	1.7899	3	242
4.0277	4.0324	10	120	1.7539	1.7530	15	431
	4.0201		210	1.6981	1.6970	6	403
3.9054	3.9033	45	021	1.6752	1.6749	4	250
	3.8883		201	1.6681	1.6687	4	520
	3.8880		002		1.6678		413
3.5658	3.5711	<1	211	1.5875	1.5884	23	423
	3.5708		012	1.5546	1.5552	19	005
	3.5679		102	1.5359	1.5345	9	234
3.1783	3.1830	100	220	1.4966	1.4967	7	600
2.9378	2.9392	93	202	1.4805	1.4795	5	343
2.7987	2.7989	18	122	1.4700	1.4703	11	025
	2.7948		212		1.4697		601
2.5993	2.5920	3	003		1.4696		404
2.4959	2.4945	12	320		1.4695		205
2.4628	2.4629	19	222	1.4200	1.4206	11	620
2.2467	2.2477	23	023	1.3992	1.3994	10	244
	2.2450		400	1.3965	1.3968	16	602
	2.2448		203	1.3819	1.3815	7	035
2.1567	2.1569	9	401	1.3346	1.3343	6	622
2.1063	2.1066	9	141	1.2949	1.2960	5	006
2.0993	2.0995	10	322	1.2667	1.2669	6	632
2.0085	2.0100	25	420	1.2449	1.2452	10	206
	2.0099		223	1.2313	1.2315	10	641
1.9592	1.9595	18	303		1.2315		444
					1.2314		245
				1.1848	1.1842	6	370

data found in the literature for vanadyl sulfate hydrates, but which can be indexed with an orthorhombic unit cell. A least-squares refinement of the powder pattern yields the following unit cell parameters: orthorhombic, $a = 8.980 \pm 0.006$, $b = 9.026 \pm 0.009$, $c = 7.776 \pm 0.003$ Å. The only systematically observed condition for the presence of reflections, $h00$: $h = 2n$, indicates as most probable space group $P2_12_12$–D_2^3 (No. 18).

The thermal dehydration properties are unusually complex, due to the number of parameters involved. Their verbal description is therefore subsequently summarized by a compilation of reaction equations. Thermogravimetrical analysis shows the water content to be variable from sample to sample between the extreme values $VOSO_4 \cdot 2.4H_2O$ and $VOSO_4 \cdot 3.5H_2O$, in contrast to the monoclinic trihydrate, which appears to be strictly stoichiometric. The variability of the water content is explicable on structural grounds and is discussed below.

Independently of the exact amount of water present, all products giving the orthorhombic diffraction pattern show in their thermogravimetric dehydration diagrams an intermediate product corresponding to the composition $VOSO_4 \cdot 2H_2O$. The first weight loss leading to this intermediate begins at about 100°C and is terminated below 210°C, whereas the last two molecules of water per formula unit are driven off between 250 and 340°C (all temperatures given are mean values from several runs, the exact individual figures being strongly dependent on experimental conditions).

Continuous high-temperature X-ray diffraction, both under linear and stepwise heating conditions, also shows the appearance of an intermediate phase in the corresponding temperature range. The product of complete dehydration of orthorhombic $VOSO_4 \cdot 3H_2O$ has in all cases been unambiguously identified as α-$VOSO_4$. For comparison, monoclinic $VOSO_4 \cdot 3H_2O$ (*7*) in well-crystallized form prepared according to (*13*), as well as in a finely divided state as obtained by partial dehydration of $VOSO_4 \cdot 5H_2O$ below 90°C, was also decomposed under varying experimental conditions.

Dynamic heating conditions with heating rates of 0.5°C/min (on the Guinier–Lenné camera) and 0.62°C/min (on the thermobalance) led for all samples to the monohydrate described by Tudo (*9*) as an intermediate product of the dehydration of the monoclinic trihydrate. However, when treated stepwise isothermally (heating by 20°C, followed by isothermal treatment during 2 hr in every step, on the Huber camera), the same phase in well-crystallized particles is found to convert into the orthorhombic polymorph around 130°C, then following the decomposition scheme of this modification. The polymorphic phase transition itself is reversible, if dehydration is avoided. This does indicate the existence of equilibrium conditions, which, however, cannot be specified due to their strong dependence on particle size. In the finely divided state, monoclinic trihydrate always starts to decompose below the phase transition temperature and therefore dehydrates as indicated in (*7*), losing two molecules of water per formula unit from about 90°C to form the monohydrate in the modification described by Ladwig (*10*).

The final product of dehydration is in all cases α-$VOSO_4$, which can be rehydrated at room temperature and relative humidities of 30–40%. This reverse reaction invariably leads to the monohydrate modification described by Tudo (*9*), and then to the monoclinic trihydrate, this latter only being hydrated further to the pentahydrate when the relative humidity exceeds 60%.

The various reactions described above can be summarized by the following equations.

Dehydration:

$$\underset{\text{all conditions}}{\mathrm{VOSO_4 \cdot 3H_2O}\ \text{(o'rhombic)}} \xrightarrow{100-210^\circ\mathrm{C}} \mathrm{VOSO_4 \cdot 2H_2O} \xrightarrow{250-340^\circ\mathrm{C}} \alpha\text{-}\mathrm{VOSO_4}, \tag{1}$$

$$\underset{\substack{\text{dynamic heating,}\\ \text{all samples}}}{\mathrm{VOSO_4 \cdot 3H_2O}\ \text{(monocl.)}} \xrightarrow{90^\circ\mathrm{C}} \underset{\text{Tudo (9)}}{\mathrm{VOSO_4 \cdot H_2O}} \xrightarrow{190^\circ\mathrm{C}} \alpha\text{-}\mathrm{VOSO_4}, \tag{2}$$

$$\begin{aligned}\underset{\substack{\text{stepwise isothermally,}\\ \text{well crystallized}}}{\mathrm{VOSO_4 \cdot 3H_2O}\ \text{(monocl.)}} &\xrightarrow{50-130^\circ\mathrm{C}} \mathrm{VOSO_4 \cdot 3H_2O}\ \text{(o'rhombic)} \xrightarrow{170^\circ\mathrm{C}} \\ &\mathrm{VOSO_4 \cdot 2H_2O} \xrightarrow{230^\circ\mathrm{C}} \alpha\text{-}\mathrm{VOSO_4},\end{aligned} \tag{3}$$

$$\underset{\substack{\text{stepwise isothermally,}\\ \text{finely divided state}}}{\mathrm{VOSO_4 \cdot 3H_2O}\ \text{(monocl.)}} \xrightarrow{90^\circ\mathrm{C}} \underset{\text{Ladwig (10)}}{\mathrm{VOSO_4 \cdot H_2O}} \xrightarrow{230^\circ\mathrm{C}} \alpha\text{-}\mathrm{VOSO_4}; \tag{4}$$

Rehydration:

$$\alpha\text{-}\mathrm{VOSO_4} \rightarrow \underset{\text{Tudo (9)}}{\mathrm{VOSO_4 \cdot H_2O}} \rightarrow \underset{\text{(monocl.)}}{\mathrm{VOSO_4 \cdot 3H_2O}} \xrightarrow{\text{humidity} > 60\%} \mathrm{VOSO_4 \cdot 5H_2O}. \tag{5}$$

$VOSO_4 \cdot 2H_2O$

The vanadyl sulfate dihydrate in a form distinctly different from that prepared under high water vapor pressure (*8*) has been found as an intermediate product in the dehydration of the orthorhombic trihydrate as described above. Although the lines of its X-ray powder diffraction pattern, given in Table III, are broadened, it can be indexed with a monoclinic unit cell. Least-squares refinement gave the following unit cell parameters: $a = 8.913 \pm 0.027$, $b = 8.93 \pm 0.09$, $c = 7.80 \pm 0.06$ Å, $\beta = 92.4 \pm 0.6°$.

Topotaxy of the Dehydration of Orthorhombic $VOSO_4 \cdot 3H_2O$

Both steps of the dehydration of orthorhombic $VOSO_4 \cdot 3H_2O$ via $VOSO_4 \cdot 2H_2O$ to α-$VOSO_4$ occur in a strictly topotactic manner. This statement is based on the following two observations: Guinier–Lenné high-temperature X-ray diffraction diagrams show a continuous, smooth transition for most of the diffraction lines from their positions in the trihydrate to those in the dihydrate, and finally in the anhydrous sulfate pattern. This behavior permits the determination of corresponding lattice planes in any of the phases involved, i.e., the determination of the topotactic orientation relations.

In the high vacuum of the transmission electron microscope and under the influence of the electron beam, the hydrate is immediately dehydrated, but under complete conservation of its external shape, i.e., to produce a pseudomorph of α-$VOSO_4$. This product is identified by its selected area electron diffraction pattern, which is clearly of the single-crystal type, being composed only of an array of sharp reflections, showing no powder ring diffraction whatsoever. This also allows the determination of the topotactic orientation, at least for the basal plane.

From these observations, the following orientation relations were deduced:

	orthorhombic $VOSO_4 \cdot 3H_2O$		$VOSO_4 \cdot 2H_2O$		α-$VOSO_4$
	(001)	parallel to	(001)	parallel to	(001)
and					
	[100]	parallel to	[100]	parallel to	$[1\bar{1}0]$.

This relative orientation of the three unit cells is illustrated in Fig. 1.

The dimensional changes associated with the dehydration are as follows:

orthorhombic $VOSO_4 \cdot 3H_2O$	$VOSO_4 \cdot 2H_2O$	α-$VOSO_4$
$a = 8.980$ Å,	$a = 8.913$ Å,	$a(2)^{1/2} = 8.854$ Å,
$b = 9.026$ Å,	$b = 8.93$ Å,	$a(2)^{1/2} = 8.854$ Å,
$c = 7.776$ Å,	$c \sin \beta = 7.79$ Å,	$c = 4.101$ Å.

This comparison shows that, when going from the trihydrate to the dihydrate, the unit cell is only slightly deformed, the unit cell volume decreasing merely from 630 to 620 Å^3, whereas in the second step of the dehydration the same applies only to the (001) basal plane, the dimensions of which remain almost unchanged, but its stacking distance being considerably shortened by 3.7 Å. These results are fully compatible with a reaction mechanism in which a two-dimensional array of atoms is conserved throughout the reaction, a frequent case in the dehydrations of crystalline hydrates (*14*).

Deduction of Structural Models for the Two New Phases

It has been demonstrated previously that results on topotactic reactions can yield the arguments required to deduce the structural principles of unknown compounds involved

TABLE III

POWDER X-RAY DIFFRACTION PATTERN OF $VOSO_4 \cdot 2H_2O$

d_{obs} (Å)	d_{calc} (Å)	I/I_0 (%)	*hkl*
7.795	7.797	86	001
5.925	5.992	26	$10\bar{1}$
	5.874		011
5.716	5.748	25	101
4.450	4.452	18	200
3.9428	3.9383	20	$20\bar{1}$
3.1480	3.1535	100	220
2.9882	2.9961	15	$20\bar{2}$
2.8666	2.8740	11	202
2.5460 d	2.5236	3	$10\bar{3}$
−2.4780	2.4956		013
	2.4882		$22\bar{2}$
	2.4754		230
2.4138	2.4170	3	222
	2.4110		$30\bar{2}$
2.2273	2.2263	8	400
2.0601	2.0603	5	411
1.9935	1.9925	13	420
1.5777	1.5768	9	440
1.5291	1.5285	<1	530
1.4849	1.4842	4	600
1.4088	1.4085	6	620
	1.4087		334

Note. d = Diffuse.

in such reactions, if at least one other structure taking part in the topotactic process is known (*15*).

This is the case here, as the crystal structure of the final product, α-$VOSO_4$, is known (*12*). It is a pronounced layer structure with alternating corner-sharing sulfate tetrahedra and tetragonal pyramids VO_5 forming the dominating layers (001), these being separated by rather long V = O . . . . V contacts, completing the distorted octahedron around the V atoms. These layers are just in that specific plane, which is conserved both orientationally and dimensionally throughout the dehydration reaction. It is therefore concluded that this very layer must be a major structural component of the two precursors in this reaction, $VOSO_4 \cdot 3H_2O$ and $VOSO_4 \cdot 2H_2O$. For a full description of the structural principles of these two hydrates, it has also to be discussed how many water molecules can be accommodated in the space available between such layers.

The approximate spatial requirements for interlayer water molecules can be estimated from known crystal structures. According to Mackenzie (*16*), a water molecule requires an area of about 7 Å^2 in a monomolecular interlayer water sheet, the thickness of which is estimated by Ladwig (*10*) to be 2.8–3.0 Å. In α-$VOSO_4$, the area occupied by one $VOSO_4$ unit is 19.6 Å^2. If we assume that the layers of this structure are essentially preexisting in the two hydrate structures discussed here, the corresponding area is 20.3 Å^2 in $VOSO_4 \cdot 3H_2O$ and 19.9 Å^2 in $VOSO_4 \cdot 2H_2O$, thus being able to accommodate three water molecules.

The decrease of the interlayer distance on dehydration of about 3.7 Å is a measure for the thickness of the water layer and indicates that this layer is either slightly corrugated or, in the case of $VOSO_4 \cdot 3H_2O$, might accommodate slightly more water than the amount corresponding to a mono-

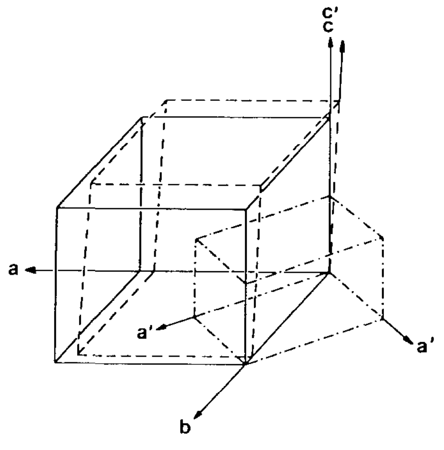

FIG. 1. Relative orientations of the unit cells of $VOSO_4 \cdot 3H_2O$ (full lines, axes *a*, *b*, *c*), $VOSO_4 \cdot 2H_2O$ (dashed lines, axes analogous), and α-$VOSO_4$ (dash-dotted lines, axes *a*′, *c*′) as found experimentally.

layer, i.e., three molecules per formula unit. This agrees with the experimental result that the water content is variable and can exceed the value three up to $VOSO_4 \cdot 3.5H_2O$.

The loss of approximately one molecule of water, leading to a composition of $VOSO_4 \cdot 2H_2O$, may enable the crystal to form a more stable arrangement of hydrogen bonds, thus adapting the structure corresponding to the unit cell of the dihydrate observed. The almost negligible change of the unit cell volume associated with this step can be understood by the fact that the dimensions within the (001) plane are essentially determined by the $VOSO_4$ substructure, whereas the water layer retains its thickness even when it is partly emptied, as the remaining water molecules require the same space in the *c* direction as in a complete layer.

It is evident that the model structures described here differ greatly from that of the monoclinic trihydrate (*7*). Whereas the latter contains dimeric molecules and thus is related to the higher hydrates, the orthorhombic form of the trihydrate and the new dihydrate both form layered structures and as such are similar to the lower hydrates and the anhydrous phases.

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