A thermal dehydration study of WO$_3$·2H$_2$O

S AYYAPPAN* and N RANGAVITTAL

Materials Research Centre and Solid State and Structural Chemistry Unit,
Indian Institute of Science, Bangalore 560 012, India

(Communicated by Professor C N R Rao)

MS received 20 August 1996

Abstract. Step-wise thermal dehydration of WO$_3$·2H$_2$O has been investigated and the various hydrated tungsten trioxide phases characterized. A cubic phase of tungsten trioxide with 0.36 moles of water is obtained by heating WO$_3$·2H$_2$O to 498 K.

Keywords. Thermal dehydration; tungsten trioxide dihydrate; cubic phase.

1. Introduction

Solid state reactions which are topochemically controlled bear orientational relationship between the parent and product phases. Except for changes in dimension in one or more directions, the atomic arrangement in the reactant crystal remains largely unaffected during the course of a topotactic solid state reaction (Rao and Raveau 1995). Gunter (1972) showed that one such reaction is the dehydration of MoO$_3$·2H$_2$O and WO$_3$·2H$_2$O to give MoO$_3$ and WO$_3$ respectively. The structural feature common to various allotropic modifications of tungsten trioxide and several of its hydrates is the presence of W$^{6+}$ in octahedral environment (Figlarz et al 1990). But the great number of possible arrangements of these octahedra, their distortions and the ease of hydration of WO$_3$ either by substitution of one oxygen of the octahedra by H$_2$O or by intercalation of H$_2$O between the sheets of the layered structure leads to a large number of structures. Among these hydrates the existence and structure of the tungsten trioxide dihydrate and monohydrate are known by the comparison of MoO$_3$·2H$_2$O (Krebs 1972) and MoO$_3$·H$_2$O (Boudjada et al 1993).

In the course of a study on the reactivity of tungsten trioxide hydrates, Gerard et al (1981) obtained a new tungsten trioxide hydrate characterized as WO$_3$·1/3H$_2$O which had similarities with the sodium octatungstate with large variations in the compositions. This hydrate crystallizes in the orthorhombic system with infinite plane of WO$_6$ octahedra sharing their corners and forming six-membered rings, which had structural relationships with the product of dehydration, a new anhydrous hexagonal tungsten trioxide (Seguin et al 1983). This hexagonal WO$_3$ phase turns irreversibly into the thermodynamically stable monoclinic WO$_3$ phase at about 673 K. A recent investigation involving the preparation and dehydration of H$_2$WO$_4$·H$_2$O has shown the presence of sodium as a requirement, with a minimum concentration of as much as 160 ppm, for the stabilization of WO$_3$·1/3H$_2$O (Pfeifer et al 1995). A new form of WO$_3$ with a pyrochlore-type structure was reported by Coucou and Figlarz (1988). This new oxide was prepared in three steps involving the thermal treatment of ammonium tungstate in acidic solution of ethylene glycol. The pyrochlore hydrate, W$_2$O$_6$·xH$_2$O,

*Author for correspondence
was then obtained by ion exchange in acidic solutions. Dehydration of these hydrates at about 373 K led to $\text{WO}_3$ in the pyrochlore structure.

From 0 K to 1273 K stoichiometric tungsten trioxide, $\text{WO}_3$, was reported to have undergone many phase transformations in the solid state (Rao and Rao 1974). Below 1173 K, $\text{WO}_3$ was tetragonal in the space group $P4/nmm$ (Kehl et al 1952) and transformed at about 1013 K into an orthorhombic modification with space group $Pmnb$. Between 290 K and 603 K, $\text{WO}_3$ exhibited monoclinic symmetry in the space group $P2_1/n$ (Loopstra and Rietveld 1977). Below 290 K, $\text{WO}_3$ was triclinic with the space group $P1$ (Diehl et al 1978) and transformed into another monoclinic phase with the space group $Pc$ at 233 K. These $\text{WO}_3$ related phases had distorted $\text{ReO}_3$ type crystal structures in common.

Figure 1. X-ray powder diffraction pattern of (a) $\text{WO}_3 \cdot 2\text{H}_2\text{O}$, (b) $\text{WO}_3 \cdot \text{H}_2\text{O}$, (c) $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$, (d) $\text{WO}_3$ (monoclinic) and (e) $\text{WO}_3$ (mixture of monoclinic and triclinic).
Although the tungstic acids or tungsten trioxide hydrates systems and their dehydra-
tion products have been extensively investigated for some time, the existence of some of
the intermediate hydrate phases remains to be understood. With this interest, we have
carried out the stepwise dehydration of \( \text{WO}_3 \cdot 2\text{H}_2\text{O} \) and studied the topotactic
mechanism involved in the reaction.

2. Experimental

Preparation of the \( \text{WO}_3 \cdot 2\text{H}_2\text{O} \) was carried out by following the procedure reported by
Freedman (1959). Fifty ml of 1·0 M \( \text{Na}_2\text{WO}_4 \) was pipetted into 450 ml of 3·0 N \( \text{HCl} \) at
373 K. The initial yellow solution turned turbid and later to a characteristic yellow
precipitate. The mixture was heated for 30 min and allowed to settle and washed
repeatedly with 0·1 N \( \text{HCl} \) at room temperature. The slurry was filtered and dried at
373 K for 2 h to obtain orange-yellow powder of \( \text{WO}_3 \cdot 2\text{H}_2\text{O} \). Atomic absorption
spectroscopy was performed to confirm the absence of Na in the final product (< 1
ppm). X-ray diffraction experiments at various temperatures were performed using
a STOE/STADIP high resolution powder X-ray diffractometer. Thermogravimetric

![Figure 2. Structural projection of \( \text{WO}_3 \cdot \text{H}_2\text{O} \).]
analysis of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ and other hydrated products was performed using POLYMER (Model STA 1500) TGA setup. Infrared spectra were recorded using the Perkin-Elmer (Model 580) spectrometer.

3. Results and discussion

High-resolution X-ray powder diffraction data of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ were collected at various temperatures. Figure 1 shows that at around 398 K the tungsten trioxide dihydrate looses one $\text{H}_2\text{O}$ molecule and converts to $\text{WO}_3 \cdot \text{H}_2\text{O}$. The X-ray diffraction

![Figure 3](image1)

**Figure 3.** Thermogravimetric analysis plot for $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$.

![Figure 4](image2)

**Figure 4.** Infrared spectra of (a) $\text{WO}_3 \cdot \text{H}_2\text{O}$ and (b) $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$. 
pattern of $\text{WO}_3 \cdot \text{H}_2\text{O}$ (figure 1b) could be indexed in the orthorhombic system (space group $Pmnb$) (Boudjada et al 1993) with the cell dimensions $a = 5.228$, $b = 10.680$ and $c = 5.128$ Å. The structure of $\text{WO}_3 \cdot \text{H}_2\text{O}$ consists of $\text{WO}_6$ octahedra which are stacked in sheets at $y = 1/4$ and $3/4$ sharing four corners in the equitorial plane, and the water
oxygen atoms alternate on the axial corners along [100] and [001] directions (figure 2). All the sheets are linked by hydrogen bonds involving the water molecules and two octahedra of neighbouring sheets. Heating $\text{WO}_3 \cdot \text{H}_2\text{O}$ to 498 K results in $\text{WO}_3 \cdot x\text{H}_2\text{O}$. The X-ray diffraction pattern of $\text{WO}_3 \cdot x\text{H}_2\text{O}$ (figure 1c) could be indexed in the cubic system with the space group $Pm3m$ with the cell dimension $a = 3.675 \text{Å}$.

Thermogravimetric analysis (figure 3) of $\text{WO}_3 \cdot x\text{H}_2\text{O}$ showed weight loss corresponding to 0.36 moles of $\text{H}_2\text{O}$ at 575 K. In figure 4, we compare the infrared spectra of $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ with that of $\text{WO}_3 \cdot \text{H}_2\text{O}$ (Daniel et al. 1987). The infrared spectrum of $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ shows a broad band around $3350 \text{cm}^{-1}$ corresponding to O–H stretching and a pronounced H–O–H deformation band at $1615 \text{cm}^{-1}$ (figure 4). The X-ray diffraction pattern corresponds to the $\text{ReO}_3$ structure consisting of corner linked $\text{WO}_6$ octahedra forming an infinite 3D network of interconnecting tunnels (figure 5a). The structure with layered sheets of $\text{WO}_6$ octahedra interleaved with $\text{H}_2\text{O}$ molecules in $\text{WO}_3 \cdot \text{H}_2\text{O}$ changes to a structure with a 3D network of $\text{WO}_6$ octahedra in $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$. The nature of the coordination of water molecule in $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ can only be studied through neutron diffraction. Heating $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ to 548 K results in the complete loss of water molecule. The X-ray diffraction pattern of the product heated at 548 K (figure 1d) corresponds to that of the stable monoclinic $\text{WO}_3$ with the space group $P2_1/n$ with the cell dimensions $a = 7.508$, $b = 7.296$, $c = 7.691 \text{Å}$ and $\beta = 90.49^\circ$. The structure of the monoclinic phase consists of distorted corner-linked $\text{WO}_6$ octahedra with the displacement of tungsten ions from the centre of the octahedra. Further heating of $\text{WO}_3$ to 673 K and then quenching it to room temperature, gives a mixture of monoclinic and triclinic phases (figure 1e). The structural projection with the monoclinic distortion is shown in figure 5b.

In summary, the present study shows that the thermal dehydration of tungsten trioxide dihydrate proceeds in three steps. All the hydrated and the final dehydrated phases have tungsten in octahedral coordination in common. The intermediate tungsten trioxide with 0.36 moles of water has a cubic symmetry.

Acknowledgements

The authors thank Prof. C N R Rao for advice and guidance. One of the authors (SA) thanks CSIR, India for the fellowship.

References

Freedman M L 1959 J. Am. Chem. Soc. 81 3834
Gunter J R 1972 J. Solid State Chem. 5 354
A thermal dehydration study of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$


