

Topotactic Dehydration of Molybdenum Trioxide-Hydrates

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It is shown that thermal dehydration of molybdenum trioxide-dihydrate proceeds in two steps, both of which are strongly topotactic. The topotactic relations have been established and been used to propose a structure model for the intermediate product, molybdenum trioxide-monohydrate, the unit cell of which has been determined.

The guiding elements of the two topotactic reactions are planes of corner-sharing octahedra. The conservation of these planes throughout the reactions is confirmed by scanning electron micrographs in addition to the results of X ray diffraction.

Introduction

In earlier literature, molybdenum trioxide-hydrates or "molybdic acids" have often been mentioned, but without sufficient characterization (1). Out of these compounds, only $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ (or H_4MoO_5) and $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (or H_2MoO_4) may be considered as definite phases.

Crystallographic data of the monohydrate are completely missing. It is, however, known that a substance of this composition is formed as an intermediate during the thermal decomposition of the dihydrate, the final product being anhydrous molybdenum trioxide. Earlier authors published results which indicate the existence of three different phases with the composition of $\text{MoO}_3 \cdot \text{H}_2\text{O}$: a yellow form, not characterized further, a white α -form, growing in well-shaped white needles, and a β -form, also as white needles, but of less pronounced shape (1). The yellow modification has been mentioned to be isotopic with $\text{WO}_3 \cdot \text{H}_2\text{O}$ (2), the crystal structure of which is, however, unknown as well.

The crystal structure of the only form of the dihydrate described up to now has recently been determined by Krebs (3) and is schematically represented by Fig. 4a and d. The unit cell is monoclinic, with $a = 10.476 \text{ \AA}$, $b = 13.822 \text{ \AA}$, $c = 10.606 \text{ \AA}$, $\beta = 91.62^\circ$, space group $P2_1/n$. The crystal structure is built up from slightly deformed layers of strongly distorted octahedra $[\text{MoO}_5(\text{H}_2\text{O})]$ sharing corners, parallel to (010).

These layers are stacked above each other with layers of crystal water in between, connected by hydrogen bonds from hydrogen atoms of water molecules coordinated to molybdenum atoms to oxygen atoms of interlayer water molecules on one hand and from hydrogen atoms of interlayer water molecules to coordinated oxygen ions on the other hand.

This structure with its two kinds of differently bound water molecules indicates the possibility of a dehydration in two steps, as it has actually been described (1, 3). It seems probable that at least the first step of the dehydration reaction, but possibly also the second, are topotactic in nature. A reaction is called topotactic, if the lattice of the solid product formed shows one or a small number of crystallographically equivalent, definite orientations relative to the lattice of the initial crystal, and if the reaction has proceeded throughout the entire volume of the initial crystal (4, 5).

The purpose of the present work was to investigate the topotactic relations in the two steps of dehydration and to collect crystallographic data of the intermediate product, molybdenum trioxide-monohydrate.

Experimental Methods

Molybdenum trioxide-dihydrate crystals were prepared by the method of Carpéni (6), often

requiring much longer crystallization times than indicated by this author.

Thermal dehydration was observed in a Mettler Thermoanalyzer TA 1 and with a focusing Guinier-Lenné high temperature powder X ray diffraction camera (Nonius, Delft).

The characterization of the different phases was based on powder X ray diffraction patterns (Guinier-de Wolff camera, $\text{CuK}\alpha$ -radiation), on single crystal X ray diffraction patterns (Weissenberg and Buerger Precession cameras), on infrared spectra recorded with a Beckman IR 12 spectrometer and on scanning electron micrographs (Stereoscan S 4, Cambridge Scientific Instruments Ltd.).

Thermal Dehydration

By thermoanalytical measurements it was found that dehydration of the dihydrate takes place in a vacuum of about 10^{-4} to 10^{-5} Torr at room temperature, leading first to the monohydrate and then to the anhydrous trioxide, the loss of water being continuous.

Dehydration in air, however, takes place in two distinct steps. The first step, from the dihydrate to the monohydrate, occurs at 60–80°C, the second step from the monohydrate to the trioxide at about 110–125°C (Fig. 1).

This clear separation of the two steps makes it possible to isolate the pure monohydrate phase and to characterize it further by infrared spectroscopy and X ray diffraction. It can unambiguously

be identified as the yellow form of $\text{MoO}_3 \cdot \text{H}_2\text{O}$, as described in (1).

Infrared Spectra

Both the infrared spectra of the dihydrate and of the monohydrate were recorded from samples prepared in potassium bromide pellets (Fig. 2). Both substances give pronounced H–O–H deformation bands at 1615 cm^{-1} . In the range of the O–H stretching frequencies, however, the two samples give very different spectra. In the case of the dihydrate, at least four peaks can be resolved in this range, occurring at 3140, 3200, 3410 and 3520 cm^{-1} , respectively. The monohydrate, in contrast, produces only one broad band at 3430 cm^{-1} in this region of the spectrum.

Maričić and Smith (7) gave for the corresponding infrared absorption bands the values 1592 and 3100 cm^{-1} for the dihydrate and 1600 and 3200 cm^{-1} for the monohydrate. The bands at 2336 and 2326 cm^{-1} , respectively, mentioned by these authors are most probably caused by the presence of carbon dioxide and have not been observed in the spectra from our samples. In view of the early date of this publication, the agreement with our results is satisfactory.

Crystallographic Data, Topotactic Relations

A single crystal of molybdenum trioxide-dihydrate has been oriented by means of Weissenberg and Precession photographs with its *b*-axis

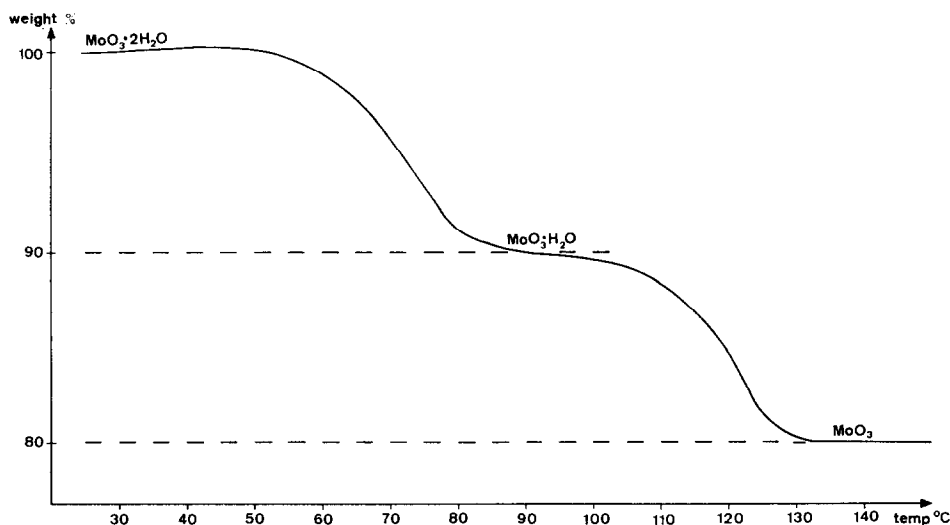


FIG. 1. Thermogravimetric curve of the dehydration of molybdenum trioxide-dihydrate (in flowing air, $0.2^3/\text{min}$).

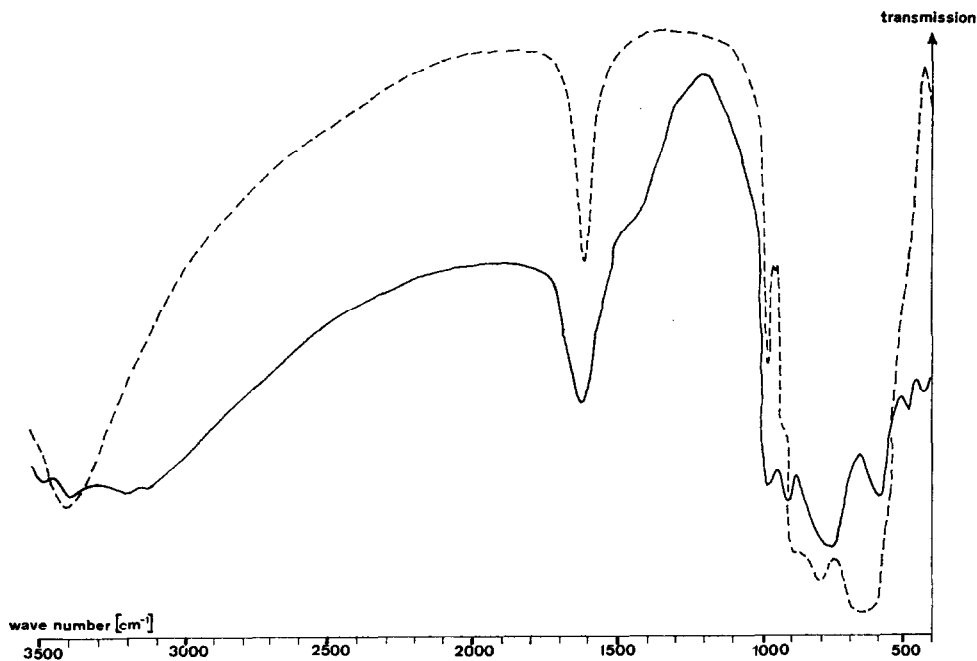


FIG. 2. Infrared spectra of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ (—) and $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (---).

parallel to the axis of a goniometer head. Its lattice dimensions are in good agreement with those given by Krebs (3).

The same crystal has then been dehydrated at 80°C in air during 3 hr to the monohydrate, without its orientation on the goniometer head being altered. The pseudomorphous product, molybdenum trioxide-monohydrate, thus obtained gave rise to X ray diffraction patterns with

TABLE I
X RAY POWDER DIFFRACTION
PATTERN OF $\text{MoO}_3 \cdot \text{H}_2\text{O}$

d	I/I_0	hkl
5.32	5	020
4.71	1	11 $\bar{1}$
3.57	4	002
3.52	3	210
3.41	5	012
3.16	1	031
3.00	1	022
2.66	1	040
2.64	3	20 $\bar{2}$
2.58	2	21 $\bar{2}$
2.52	1	032
2.32	1	31 $\bar{1}$
2.09	1	123
2.05	1	142
1.98	1	312
1.84	2	250
1.81	3	340
1.78	1	251
1.71	1	024
1.65	1	25 $\bar{2}$ /124
1.62	1	402

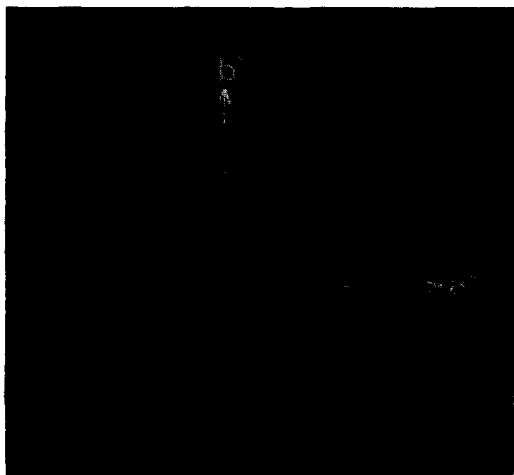


FIG. 3. Precession photograph ($hk0$) of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ pseudomorph.

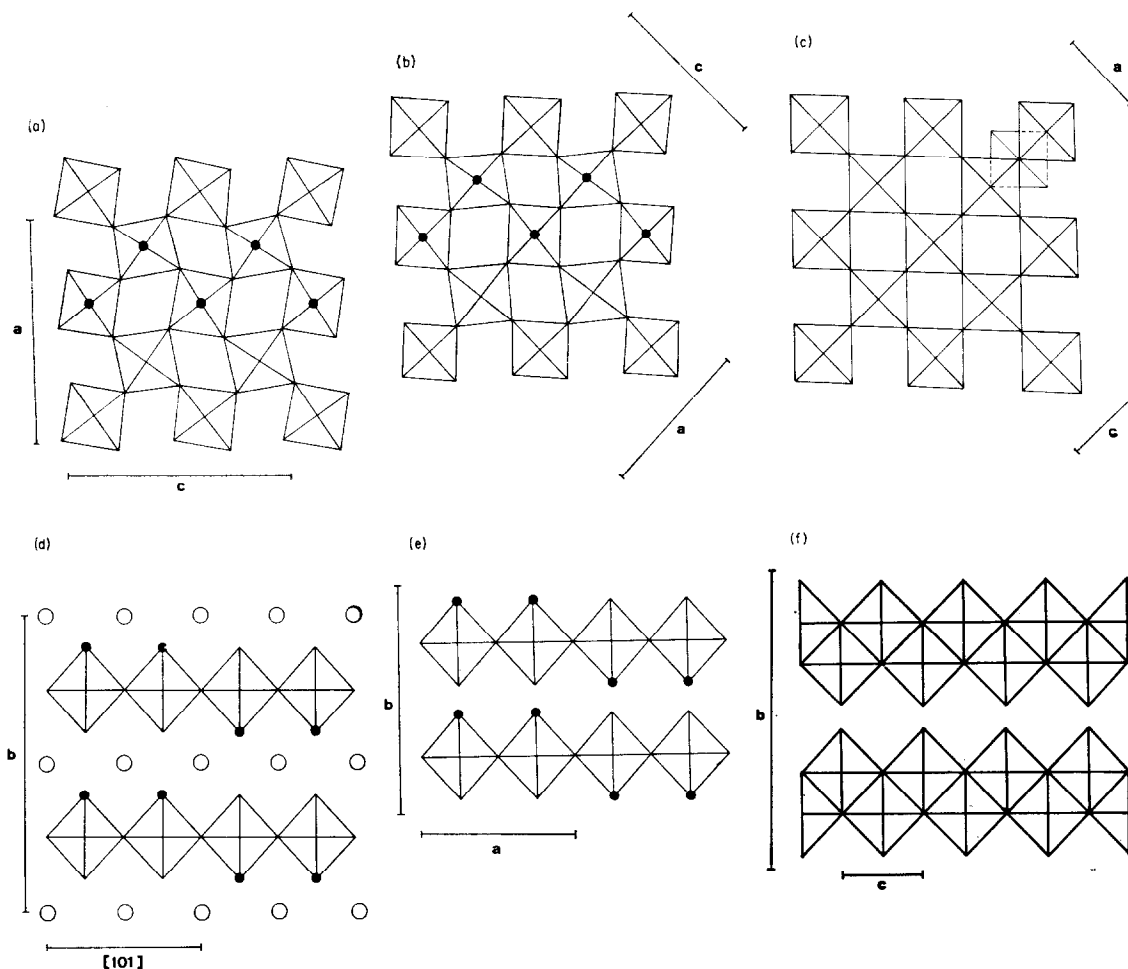


FIG. 4. Comparison of the schematic structures involved in the topotactic dehydration of molybdenum trioxide-dihydrate: (●) coordinated H_2O ; (○) interlayer H_2O . (a) Layer (010) of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, octahedra $[\text{MoO}_5(\text{H}_2\text{O})]$; (b) layer (010) of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (proposed structure), octahedra $[\text{MoO}_5(\text{H}_2\text{O})]$; (c) layer (010) of MoO_3 , octahedra $[\text{MoO}_6]$; (d) projection (101) of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, octahedra $[\text{MoO}_5(\text{H}_2\text{O})]$; (e) projection (001) of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (proposed structure), octahedra $[\text{MoO}_5(\text{H}_2\text{O})]$; (f) projection (100) of MoO_3 , octahedra $[\text{MoO}_6]$.

broadened reflections, but similar to single crystal patterns (e.g., Fig. 3). Therefrom, the following unit cell dimensions of the yellow molybdenum trioxide-monohydrate could be determined:

$$\begin{aligned} a &= 7.55 \text{ \AA} \\ b &= 10.69 \text{ \AA} \\ c &= 7.28 \text{ \AA} \\ \beta &= 91^\circ \end{aligned}$$

The systematic extinctions observed indicate the most probable space group to be $P2_1/c$.

The powder X ray diffraction pattern of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ has been indexed based on these constants, although the broadened reflections

cannot be measured to the usual accuracy (Table I).

The relation between the two structures involved in the reaction $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ (Di) \rightarrow $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (Mono) + H_2O can be described as:

$$\begin{aligned} (010)_{\text{Di}} &\parallel (010)_{\text{Mono}} \\ [\bar{1}01]_{\text{Di}} &\parallel [001]_{\text{Mono}} \\ [101]_{\text{Di}} &\parallel [100]_{\text{Mono}} \end{aligned}$$

with the plane (010) remaining virtually unchanged in its dimensions:

$$\begin{aligned} d_{(101)\text{Di}} &= 7.3 \text{ \AA}, & d_{(001)\text{Mono}} &= 7.28 \text{ \AA}, \\ d_{(101)\text{Di}} &= 7.55 \text{ \AA}, & d_{(100)\text{Mono}} &= 7.55 \text{ \AA}, \end{aligned}$$

whereas the interlayer distance decreases by 22.65% from $13.82/2$ to $10.69/2 \text{ \AA}$.

Further dehydration of the oriented pseudomorph at 200°C on the goniometer head, keeping its initial orientation, yielded anhydrous molybdenum trioxide, also pseudomorphous, with the known lattice constants of this compound ($a = 3.96 \text{ \AA}$, $b = 13.86 \text{ \AA}$, $c = 3.70 \text{ \AA}$) (8).

The topotactic relation for this second step of the reaction can only approximately be given, as at the relatively high temperature of 200°C small shifts of the crystal on its support occur. The relations can be described as:

$$\begin{aligned} (010)_{\text{Mono}} &\parallel (010)_{\text{Anhydr}} \\ [100]_{\text{Mono}} &\parallel [001]_{\text{Anhydr}} \\ [001]_{\text{Mono}} &\parallel [100]_{\text{Anhydr}} \end{aligned}$$

This means that again the dimensions of the layer (010) are only slightly altered, suffering a slight expansion in both axial directions and an increase in symmetry, as the formerly slightly oblique angle changes into a right angle and both axes are halved. Again the change in b , the inter-layer distance, is much more pronounced.

In molybdenum trioxide, the coordination octahedra partly share edges instead of corners only (8), which explains the change in the lattice constants and in symmetry.

From the close relation in lattice constants and in orientation of molybdenum trioxide-mono-hydrate, both to the dihydrate and to the anhydrous trioxide, it must be assumed that all three crystal structures show close analogy. Thus, based on considerations of topotaxy, a crystal structure may be proposed for the mono-hydrate. It consists of layers of octahedra $[\text{MoO}_3(\text{H}_2\text{O})]$, sharing corners, similar to the layers of the dihydrate structure, being stacked on top of each other and connected by hydrogen bonds from water molecules coordinated to molybdenum atoms in one layer to oxygen ions in the next layer.

The structural relations between the structure of the dihydrate, the proposed structure of the mono-hydrate and the structure of the anhydrous trioxide, governing both steps of the dehydration reaction, are illustrated in Fig. 4.

Morphology

As both molybdenum trioxide-hydrates dehydrate rapidly in vacuum, it has not been possible to investigate these crystals by scanning electron microscopy. However, optical microscopy shows that the initial crystals of the

dihydrate form rectangular prismatic particles of up to 1 mm in length, with highly reflecting surfaces. When decomposed to the mono-hydrate, the crystals lose their surface lustre, indicating the presence of microscopical cracks.

The final product, pseudomorphous anhydrous molybdenum trioxide, has been photographed in the scanning electron microscope. The photographs (Fig. 5) clearly show series of parallel cracks, causing the original crystals to disintegrate, yielding an arrangement of parallel lamellae. Photographs of a crystal previously oriented by X ray diffraction experiments prove the orientation of the lamellae to be (010) of the dihydrate and subsequently also (010) of the mono-hydrate and of the anhydrous trioxide. In view of the fact that the (010) plane remains rather undisturbed by dehydration, this is in good agreement with the crystallographic results given above.

Discussion

From the crystallographic and morphological results it is obvious that both steps of the dehydration reaction of molybdenum trioxide-dihydrate are strongly topotactic. In accordance with results of investigations on decomposition reactions of other substances crystallizing in layer lattices (5), the structural element controlling



Fig. 5. Scanning electron micrograph of molybdenum trioxide, pseudomorphous after molybdenum trioxide-dihydrate. Orientation of lamellae: (010). 130 \times .

these reactions is a plane, and the formation of the new phases is controlled by nucleation on inner lattice planes (9). The morphological results clearly demonstrate that nucleation occurs on many different sites within one and the same crystal and that the reaction does not proceed from one single nucleus throughout the volume of the crystal.

In the present case, considerations of the topotactic reactions led to the possibility of proposing a structure for molybdenum trioxide-mono hydrate, which would not have been possible without these results.

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