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On the Thermal Decomposition of Molybdenum Trioxide *in vacuo*

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When heated in evacuated, sealed silica tubes at temperatures between 550° and 800° C molybdenum trioxide has been found to undergo partial decomposition forming various lower molybdenum oxides. Among the latter are two previously unknown compounds, ζ- and η-molybdenum oxide, which have been characterized by their X-ray powder patterns.

In connection with studies on various molybdenum oxides carried out at this Institute it was observed that molybdenum trioxide decomposes when heated in evacuated, sealed silica tubes at red heat. After the heat treatment the trioxide crystals were slightly contaminated by dark blue or bluish-violet particles. Previous authors have also reported that molybdenum trioxide is unstable at reduced pressures of oxygen. Thus Nydahl [1] observed that molybdenum trioxide, when sublimed in a stream of air at about 800° C, gives partly reduced bluish products, while preparations obtained at the same temperature by sublimation in oxygen are colourless or faintly yellow. Decomposition of molybdenum trioxide in the electron microscope has been reported by König [2, 3], who observed the formation of dioxide during this process, and by Glemser and Lutz [4], who found the decomposition products to contain the oxides Mo_4O_{11}, Mo_8O_{23}, Mo_9O_{26}, and probably MoO_2. Studies on the thermal decomposition of tungsten trioxide have previously been carried out at this Institute [5].

In order to make sure that no reducing material was present, our experiments were carried out using molybdenum trioxide which had been sublimed in a stream of oxygen at about 800° C*. The heat treatment was performed in silica tubes which had been preheated in a stream of oxygen for several hours at 900° C. The reaction tubes containing the molybdenum trioxide samples were evacuated by means of a rotary oil pump, a cold trap with liquid air being attached to the pump, and sealed in a gas oxygen flame.

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* A finely ground specimen of this preparation was found to have grown appreciably darker than a freshly powdered sample after preservation for a few months in a covered weighing bottle kept in the laboratory.

The heat treatment was carried out in an electric furnace. In order to reduce the temperature gradient within the reaction tubes they were kept in holes bored in a heavy cylindrical block of fire-resisting steel. This block was covered with a steel lid and vertically inserted in the furnace. A platinum-platinum rhodium thermocouple was introduced in one of the holes of the cylinder through a narrow opening in the lid. The variation of the temperature during an experiment did not exceed ± 5° C. The samples were quenched in water from the reaction temperature.

The preparations were investigated under the microscope. Concentrated samples of the reduced material were obtained by picking out the dark particles. The phases forming relatively large crystals, *viz.* Mo_8O_{23} and Mo_9O_{26}, were readily isolated in this way, while the enrichment of those occurring in very small crystals offered some difficulties. Attempts to perform the separation of the phases chemically, *e.g.* by means of ammonia, were less successful. The various phases were identified by means of X-ray powder photographs taken in a Guinier focusing camera using Cu-$K\alpha$ radiation. Sodium chloride was always added to the powder specimens as an internal standard ($a_{NaCl} = 5.6398$ Å). A survey of the results of the phase analyses of several preparations is given in Table 1.

Table 1. Phase analysis of preparations obtained by heating molybdenum trioxide in evacuated, sealed silica tubes.

Heating temperature	Heating time	Phases identified by microscopical examination	Phases identified by powder photographs
549° C	87 hours	MoO_3 crystals + small amount of irregular bluish-black aggregates, consisting of extremely thin, fragile plates	MoO_3 + η-oxide
608° C	46 hours	MoO_3 crystals + aggregates of dark crystals	MoO_3 + η-oxide
650° C	44 hours	MoO_3 crystals + prismatic, blue-violet crystals or crystal aggregates of high brilliance	MoO_3 + Mo_8O_{23}
700° C	46 hours	—"— —"— —"—	MoO_3 + Mo_8O_{23}
722° C	42 hours	—"— —"— —"—	MoO_3 + Mo_9O_{26}
803° C	42 hours	Highly discoloured, greyish-black MoO_3. (An extremely small amount of a bluish-black phase isolated by treatment with ammonia)	MoO_3

In all cases the quantity of reduced material in the samples was very small in comparison with the amount of undecomposed trioxide, but generally seemed to increase with increasing heating temperature as long as the melting point of the preparations was not exceeded. The main portion of the reduced substance generally appeared in the top layer of the trioxide samples.

After heating at high temperatures (below the melting temperature) the molybdenum trioxide appeared in discoloured, greyish-blue or green crystals which, however, gave powder patterns very similar to those obtained from trioxide crystals of normal appearance. Thus only some minor variations of the intensities of the lines could be observed which may be attributed to

Table 2. Powder pattern of ζ-molybdenum oxide. ($MoO_{2.88}$ heated at about 600° C for 2 days.)

I	*d* Å	*I*	*d* Å
w	7.25	vw	2.562
w	4.02	vw	2.520
vw	3.91	vw	2.319
s	3.58	vw	2.307
vw	3.51	w	2.299
s	3.36	vw	2.288
s-	3.27	vw (diffuse)	2.169
vw	3.11	vw (diffuse)	2.102
vw	3.05	m	1.989
vw	2.771	w (diffuse)	1.960
vw	2.710	m	1.869
w	2.603		

orientation effects. At present it is not possible to conclude whether the reason for this change of colour is the existence of an extended homogeneity range of the trioxide structure or the formation of another phase (*cf.* the discussion of the thermal decomposition of tungsten trioxide [5]).

Samples heated above the melting temperature formed a greyish-black mass from which it was not possible to separate the constituents by picking out crystals. By treating with dilute ammonia the molybdenum trioxide was dissolved, leaving an extremely small residue of a bluish-black substance. However, the quantity of this material was too small to allow a powder photograph to be taken.

In spite of the care given to the experimental conditions it was very difficult to obtain reproducible results in some cases. Thus some of the preparations obtained definitely did not correspond to a state of equilibrium. A sample heated at 680° C for 72 hours was found to contain MoO_3, Mo_8O_{23} and another oxide phase (ζ-molybdenum oxide) which has also been prepared by heating a mixture of molybdenum and molybdenum trioxide of the gross composition $MoO_{2.88}$ at about 600° C *in vacuo*. In a molybdenum trioxide sample heated at 753° C for 45 hours Mo_9O_{26} as well as Mo_4O_{11} could be identified in the powder

Table 3. Powder pattern of η-molybdenum oxide, obtained by heating molybdenum trioxide in vacuo at 608° C.

I	*d* Å
vw	6.04
s	3.92
m	3.60
w	3.39
vw	3.34
vw	2.811
w	2.717
w	2.669

patterns in addition to the trioxide. Similar difficulties in reaching a state of equilibrium have also been observed previously in connection with attempts to prepare the oxides Mo_8O_{23} and Mo_9O_{26} in a pure state by heating molybdenum metal and trioxide *in vacuo*[6]. Due to the difficulties in performing the phase analyses it cannot at present be definitely concluded whether or not the samples listed in Table 1 correspond to states of equilibrium.

However, the experiments show that molybdenum trioxide undergoes a partial decomposition under the conditions applied. As the presence of reducing material was carefully avoided it seems most likely that the trioxide is unstable in the temperature interval 550°—800° C at a reduced pressure of oxygen. Two previously unknown molybdenum oxides have been observed during the experiments and preliminarily designated with the symbols ζ-molybdenum oxide and η-molybdenum oxide. Powder patterns which are likely to represent fairly pure samples of these two oxides are listed in Table 2 and 3. These serve to complement the powder data on molybdenum oxides previously reported from this Institute[7].

The molybdenum oxides known at present are thus MoO_3[8-10], Mo_9O_{26}[11], Mo_8O_{23}[11], Mo_4O_{11}[12], MoO_2[13], and Mo_3O[14], the crystal structures of which have been determined, and the ε-[5], ζ-, and η-oxides of unknown compositions and structures. Further studies on the molybdenum-oxygen system are in progress.

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