The Thermal Decomposition of Ammonium Polymolybdates. II

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It was reported in a foregoing paper[1] that the weight-decrease curves and the ammonia evolution curves of ammonium dimolybdate, ammonium heptamolybdate, ammonium octamolybdate and ammonium trimolybdate are step-like. A certain crystal structure should correspond to each stage of these curves. The present paper, therefore, deals with the structural change in the process of thermal decomposition.

Experimental

Chemical Analysis.—The starting materials and their decomposition products were chemically analyzed; the quantity of molybdenum was determined by gravimetric analysis, using lead acetate, and that of ammonia, by the Kjeldhal method. The starting materials were found to be in agreement with these empirical formulae: $(NH_4)_2O\cdot 2MoO_3$ for dimolybdate, $3(NH_4)_2O\cdot 7MoO_3\cdot 4H_2O$ for heptamolybdate, $2(NH_4)_2O\cdot 8MoO_3\cdot 2H_2O$ for octamolybdate, and $(NH_4)_2O\cdot 3MoO_3\cdot xH_2O$ for trimolybdate,

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[1] E. Ma, This Bulletin, 37, 171 (1964).

where x depends upon the condition of preparation.

Differential Thermal Analysis.—The differential thermal analysis was performed in air at a heating rate of 7~10°C/min. The reference junction of the differential couple was embedded in inert fused quartz. Fifty milligrams of the sample was sandwiched between two layers of about 300 mg. of the fused quartz in a platinum cell. The thermo-couple employed was alumel-chromel.

X-Ray Analysis.—The X-ray diffraction powder patterns were taken by a Guinier focussing camera using Cu$K\alpha$ radiation. The powder patterns of the starting materials were reported on in the foregoing paper.

Results and Discussion

As is usual with differential thermal analysis, the peaks indicate the temperature at which reaction actually ends. The beginning of the reaction corresponds to a cross-point of the straight-line parts of the base line and the relevant peak. Thermograms of ammonium hepta-, di-, octa- and trimolybdates are given in Fig. 1 for purposes of comparison. They give characteristic thermograms and exhibit good reproducibility. Three endothermic peaks are observed for ammonium heptamolybdate tetrahydrate, at 130, 245, and 355°C. Also, three endothermic peaks are observed for ammonium dimolybdate, at 225, 255 and 355°C. Two endothermic peaks are observed for ammonium octamolybdate dihydrate, at 287 and 377°C. Five endothermic peaks are observed for ammonium trimolybdate, at 98, 145, 200, 358, and 375°C. Two exothermic peaks are observed for the trimolybdate, at 255 and 425°C.

Ammonium Heptamolybdate Tetrahydrate.—The X-ray diffraction pattern of ammonium heptamolybdate tetrahydrate, Fig. 2a, does not change until 130°C, the first endothermic peak. At 130°C the crystal lattice of the heptamolybdate collapses, and a new, previously unknown structure appears (Fig. 2b). This structure, which will be called pattern A hereafter, is obtained in the temperature range from 130 to 245°C. The decomposition product corresponding to pattern A was identified as $2(NH_4)_2 \cdot O \cdot 5MoO_3$ through chemical analysis. At 245°C, the second endothermic peak, pattern A changes into another pattern which is identical with the pattern of octamolybdate (Fig. 2c). The octamolybdate is obtained in the temperature range from 245 to 355°C, and it is followed by the pattern of molybdenum trioxide above 355°C (Fig. 2d), which corresponds to the last endothermic peak.

A correlation of the differential thermal analysis curve, the weight decrease curve, and the deammoniation curve in the case of ammonium heptamolybdate tetrahydrate is shown in Fig. 3. The three endothermic peaks in the differential thermal analysis curve correspond to the stages in the weight decrease curve

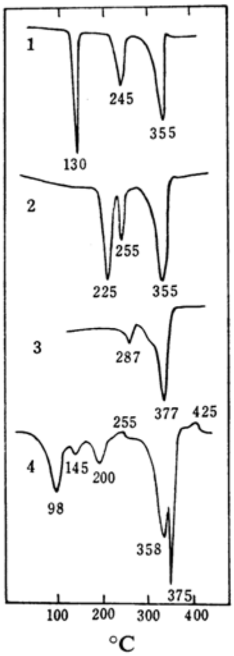

Fig. 1. Differential thermal analysis curves.
1) Ammonium heptamolybdate tetrahydrate
2) Ammonium dimolybdate
3) Ammonium octamolybdate dihydrate
4) Ammonium trimolybdate tetrahydrate

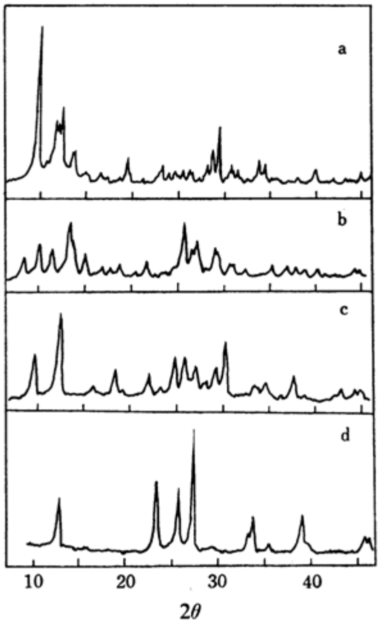

Fig. 2. X-Ray powder patterns.
a) Ammonium heptamolybdate tetrahydrate
b) Pattern A
c) Octamolybdate
d) Molybdenum trioxde

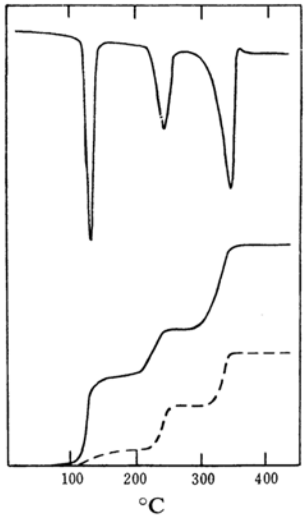

Fig. 3. Ammonium heptamolybdate tetrahydrate.

and in the deammoniation curve, and they are in good agreement. The endotherm at 130°C is referred principally to dehydration, which results in the structural change from ammonium heptamolybdate tetrahydrate to pattern A. Since dehydration does not proceed step-by-step in this case, and since most of the water is lost without resulting in any structural change, they may be regarded as of the zeolitic type. When, however, dehydration proceeds to completion, structural change does occur. The rest of the water, in consequence, must have an important role in constructing the crystal structure. The endotherm at 255°C corresponds to the deammoniation which results in the structural change from pattern A to octamolybdate. The endotherm at 355°C corresponds to the change from octamolybdate to molybdenum trioxide through further deammoniation.

Thus, ammonium heptamolybdate tetrahydrate changes upon heating in the following manner;

$$3(NH_4)_2O\cdot7MoO_3\cdot4H_2O \xrightarrow[\text{115∼130°C}]{} 2(NH_4)_2O\cdot5MoO_3 \xrightarrow[\text{225∼245°C}]{} 2(NH_4)_2O\cdot8MoO_3 \xrightarrow[\text{320∼355°C}]{} MoO_3$$

The results obtained by previous authors are given below for the purpose of comparison:

Funaki:[2] $3(NH_4)_2O\cdot7MoO_3\cdot4H_2O \xrightarrow[\text{110°C}]{} 3(NH_4)_2O\cdot7MoO_3 \xrightarrow[\text{200°C}]{} (NH_4)_2O\cdot4MoO_3 \xrightarrow[\text{280°C}]{} MoO_3$

Duval:[3] $3(NH_4)_2O\cdot7MoO_3\cdot4H_2O \xrightarrow[\text{50∼90°C}]{} 2(NH_4)_2O\cdot5MoO_3 \xrightarrow[\text{140∼200°C}]{} (NH_4)_2O\cdot4MoO_3 \xrightarrow[\text{270∼340°C}]{} MoO_3$

Hegedüs:[4] $3(NH_4)_2O\cdot7MoO_3\cdot4H_2O \xrightarrow[\text{110∼150°C}]{} 2(NH_4)_2O\cdot5MoO_3 \xrightarrow[\text{210∼255°C}]{} (NH_4)_2O\cdot4MoO_3 \xrightarrow[\text{350∼400°C}]{} MoO_3$

Rode:[5] $5(NH_4)_2O\cdot12MoO_3\cdot12H_2O \xrightarrow[\text{125°C}]{} 5(NH_4)_2O\cdot12MoO_3 \xrightarrow[\text{220°C}]{} 2(NH_4)_2O\cdot5MoO_3 \xrightarrow[\text{250∼265°C}]{} (NH_4)_2O\cdot4MoO_3 \xrightarrow[\text{320∼370°C}]{} MoO_3$

Ammonium Dimolybdate. — In the case of ammonium dimolybdate, the room temperature pattern, Fig. 4a, is preserved until 225°C, the first endothermic peak, and is transformed into a previously unknown structure which has a narrow stability range of 225∼255°C. The powder pattern of the structure will be called pattern B. At 225°C, the second endothermic peak, another structure begins to appear; this structure is crystallographically identical with the octamolybdate, Fig. 4c. The pattern of

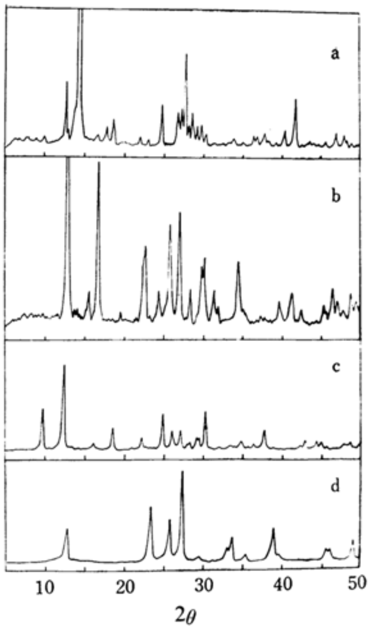

Fig. 4. X-Ray powder patterns.
- a) Ammonium dimolybdate
- b) Pattern B
- c) Octamolybdate
- d) Molybdenum trioxide

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[2] K. Funaki and T. Segawa, *J. Electrochem. Soc. Japan* (*Nippon Denkikagaku Zasshi*), **18**, 152 (1950).

[3] C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier, Amsterdam (1953), p. 332.

[4] A. J. Hegedüs, K. Sasvari and J. Neugebauer, *Z. anorg. u. allgem. Chem.*, **293**, 56 (1957).

[5] E. Ya. Rode and V. N. Tverdokhlebov, *Zhur. Neorg. Khim.*, **3**, 2343 (1958).

the octamolybdate is observed in the temperature range from 255 to 335°C and is followed by the pattern of molybdenum trioxide above 355°C, the last endothermic peak (Fig. 4d).

A correlation of the differential thermal analysis curve, the weight decrease curve and the deammoniation curve is shown in Fig. 5. The inflection around 225°C in the weight decrease curve is indicative of a decomposition product with a narrow stability range. Deammoniation until the inflection gives rise to the first endothermic peak at 225°C. The second endothermic peak is, therefore, due to deammoniation from the inflection to the plateau. The plateau in the weight decrease curve between 250 and 320°C corresponds to the octamolybdate. The endotherm at 355°C corresponds to further deammoniation, which results in the change from the octamolybdate to molybdenum trioxide.

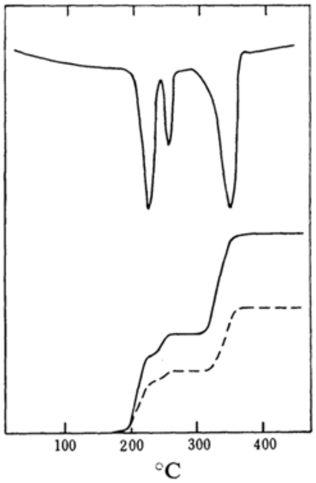

Fig. 5. Ammonium dimolybdate.

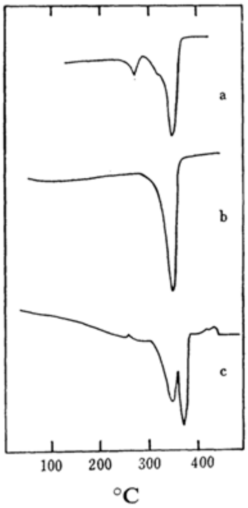

Fig. 6. Differential thermal analysis curves of ammonium octamolybdates.

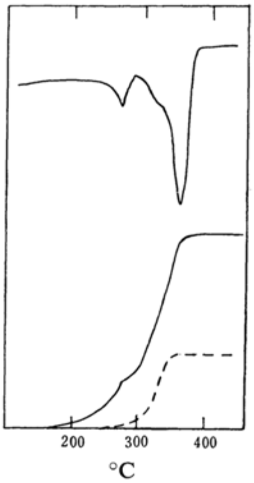

Fig. 7. Ammonium octamolybdate dihydrate.

Ammonium Octamolybdate. — Figure 6 shows thermograms of three sorts of ammonium octamolybdates of different origins. Figure 6a is octamolybdate dihydrate from an aqueous solution, Fig. 6b is anhydrous ammonium octamolybdate prepared through the calcination of ammonium heptamolybdate tetrahydrate, and Fig. 6c is one prepared through the calcination of ammonium trimolybdate. These three octamolybdates, notwithstanding their non-coincidence in thermogram, give the same X-ray powder pattern as well as the same mole ratio of $(NH_4)_2O : MoO_3 = 1 : 4$ upon chemical analysis. All the octamolybdates change into molybdenum trioxide around 370°C, at the strong endothermic peak. A correlation of the differential thermal analysis curve, the weight decrease curve and the deammoniation curve of ammonium octamolybdate dihydrate is shown in Fig. 7. The endotherm at 287°C is referred mainly to dehydration, which results in no structural change. It is an outstanding feature of the octamolybdate that no endotherm which can be referred to dehydration appears around 100°C. Accordingly, the water of crystallization in this case must be of a different character from that in the case of heptamolybdate. As one of five water molecules of copper sulfate pentahydrate is held up to 250°C, so the water molecules in the case of the octamolybdate must be tenaciously held through the hydrogen bond.

Ammonium Trimolybdate.—The existence of the trimolybdate as a chemical species has not yet been confirmed. Lindqvist has suggested the possibility that the trimolybdate is actually double-salts of hepta- and octamolybdates.[6] The X-ray examination of a sample with the chemical composition of trimolybdate illustrates that octamolybdate is predominant and that a previously unidentified pattern exists as an auxiliary part instead of the heptamolybdate. The trimolybdate has been found to change into an intermediate molybdate, $(NH_4)_2O \cdot 3.5MoO_3$, after two months of standing still and into the octamolybdate after another half-year. The auxiliary part in the powder pattern also definitely diminished in strength after two months, finally disappearing in half a year. Therefore, the starting material might have included some volatile ammonium molybdate, the normal ammonium molybdate, for instance. The first and second endothermic peaks, at 99°C and 146°C are due to dehydration. The powder pattern of the trimolybdate does not change until 200°C, the third endothermic peak, above which the pattern becomes exclusively that of the octamolybdate. The exothermic peak at 255°C is due to the crystallization of the octamolybdate. The last endothermic peak is resolved into two maxima. Above 358°C, the first maximum, molybdenum trioxide is produced, while the octamolybdate is still predominant. Above 375°C, the second maximum, the molybdenum trioxide becomes predominant and the octamolybdate, auxiliary. Above 425°C, the exothermic peak which corresponds to the crystallization of the molybdenum trioxide, the formation of the molybdenum trioxide is complete. A correlation of the differential thermal analysis curve, the weight decrease curve and the deammoniation curve of the ammonium trimolybdate is shown in Fig. 8.

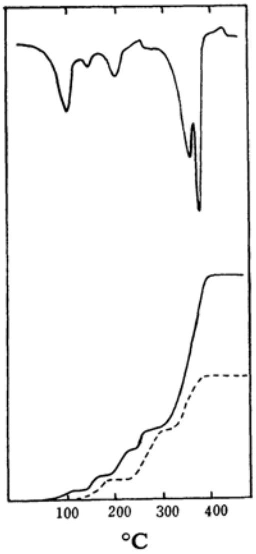

Fig. 8. Ammonium trimolybdate.

Change of Color.—The color of the final decomposition product obtained in air is yellow above 350°C and pale grey-green when cooled to room temperature, while that of the final product in vacuo is purple-black, and this does not change when the product is cooled to room temperature. In respect to the color change during the thermal decomposition, there is little difference among various kinds of polymolybdates. The X-ray investigation revealed that the purple-black oxide is a mixture of MoO_3, Mo_8O_{23}, Mo_9O_{26}, and Mo_4O_{11}, as has been reported in the foregoing paper.[7] The purple-black color may be referred to an oxygen deficiency. When the purple-black oxide, the decomposition product in vacuo, was heated again in air, it became yellow above 350°C, and a slight increase in weight was observed. The change of color in air and in vacuo is given in Tables I and II.

TABLE I. CHANGE OF COLOR IN AIR

100°C	200°C	300°C	400°C	500°C
White	Light grey-green	Yellow green	Yellow	Golden yellow

TABLE II. CHANGE OF COLOR IN VACUO

20°C	70°C	100°C	200°C	250°
White	Light green	Yellow green	Dark yellow-green	Purple-black

Summary

The thermal decomposition of ammonium di-, hepta-, tri- and octamolybdates has been investigated by means of differential thermal analysis, chemical analysis, and X-ray diffraction techniques. The steps of the decomposition may be described as follows:

Heptamolybdate

$$3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O \xrightarrow[130°C]{} 2(NH_4)_2O \cdot 5MoO_3 \xrightarrow[245°C]{} 2(NH_4)_2O \cdot 8MoO_3 \xrightarrow[360°C]{} MoO_3$$

Dimolybdate

$$(NH_4)_2O \cdot 2MoO_3 \xrightarrow[226°C]{} (NH_4)_2O \cdot 3MoO_3 \xrightarrow[225°C]{} 2(NH_4)_2O \cdot 8MoO_3 \xrightarrow[360°C]{} MoO_3$$

Octamolybdate

$$2(NH_4)_2O \cdot 8MoO_3 \cdot 2H_2O \xrightarrow[287°C]{} 2(NH_4)_2O \cdot 8MoO_3 \xrightarrow[370°C]{} MoO_3$$

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[6] I. Lindqvist, *Nova Acta Reg. Soc. Sci. Upsal., Ser. IV*, 15, 7 (1950).

[7] Cf. Ref. 1.

Trimolybdate

$(NH_4)_2O \cdot 3MoO_3 \cdot xH_2O \xrightarrow[200^\circ C]{} 2(NH_4)_2O \cdot 8MoO_3 \xrightarrow[370^\circ C]{} MoO_3$

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