# *The Thermal Decomposition of Ammonium Polymolybdates. I*

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(Received August 6, 1963)

When a normal ammonium molybdate solution is acidified, various polyanions of increasing degrees of condensation are obtained according to different acidifications and other conditions.[1] Gmelin[2] has reported the existence of nine kinds of molybdates with different mole ratios of $R_2O$: $MoO_3$. In ammonium polymolybdates of various compositions, the structures of the heptamolybdate (paramolybdate) ion and the octamolybdate (tetramolybdate) ion have been crystallographically investigated by Lindqvist.[3] Little is known about the crystal structures of the rest. The present paper is concerned with four of them, ammonium di-, hepta-, tri- and octa-molybdate; the thermal decomposition of each has also been studied.

The thermal decomposition of ammonium heptamolybdate has previously been studied by several authors, Duval[4] using thermogravimetric analysis and Hegedüs et al.,[5] using X-ray diffraction techniques besides thermogravimetric analysis. Funaki and Segawa[6] reported the thermal decomposition of several kinds of polymolybdates, but they gave no description on the experimental method employed. A differential thermal analysis of the thermal decomposition of ammonium tetra-, para- and normal-molybdate has been reported by Rode and Tverdokhlebov.[7] Rode and Tverdokhlebov, however, adopted for heptamolybdate (paramolybdate) an empirical formula, $5(NH_4)_2O\cdot 12MoO_3\cdot 12H_2O$, which has been proved incorrect; an alternative formula, $3(NH_4)_2O\cdot 7MoO_3\cdot 4H_2O$, had long been supported by crystallographic studies.[8] The tetramolybdate in their paper, $(NH_4)_2O\cdot 4MoO_3\cdot 2H_2O$, is essentially identical with octamolybdate, $(NH_4)_4Mo_8O_{26}\cdot 4H_2O$, the crystal structure of which has been determined by Lindqvist. Previous works of crystallographic significance seem to have been ignored in their paper. The behaviors of ammonium polymolybdates in the thermal decomposition are comparable with those of ammonium polytungstates, since they are both ammonium salts of the polyacid of transition elements in the sixth group of the periodic table. Reference may be made to a previous work on the thermal decomposition of ammonium paratungstate.[9] In the present paper the thermal decomposition of ammonium polymolybdates is treated by means of thermogravimetric analysis, ammonia determination and omegatron mass-spectrometry; in a succeeding paper studies by means of differential thermal analysis and X-ray diffraction techniques will be reported.

## Experimental

**Chemical Analysis.**—Samples of ammonium dimolybdate, heptamolybdate, trimolybdate and octamolybdate were first identified as such by determining their compositions through chemical analysis. The quantity of molybdenum was determined by the gravimetric method, using lead acetate, and that of ammonia, by the Kjeldhal method. The results were found to be in agreement with the 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, where $x$ depends upon conditions of preparation.*

**X-Ray Analysis.**—Samples of ammonium heptamolybdate and octamolybdate, the lattice constants of which had been known,[10] were further identified as such by crystallographic data of single crystals using rotation photographs. The unit cell dimensions for ammonium heptamolybdate are: $a=8.382$Å $b=36.125$Å, $c=10.464$Å and $\beta=116°0'$, while those for octamolybdate are: $a=7.76$Å, $b=9.75$Å, $c=9.78$Å, $\alpha=97°2'$, $\beta=100°5'$ and $\gamma=98°$. X-Ray diffraction patterns were taken by a Guinier focussing camera using Cu$K\alpha$ radiation. The

1) I. Lindqvist, *Nova Acta Reg. Soc. Sci. Upsal. Ser. IV*, 15 (1950), I. Lindqvist, *Acta Chem. Scand.*, **5**, 568 (1951).
2) Gmelin, "Handbuch der Anorganischen Chemie," Nr. 53, Verlag Chemie G. m. b. H., Weinheim (1935), p. 113.
3) I. Lindqvist, *Arkiv Kemi*, **2**, 325, 349 (1950).
4) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier, Amsterdam (1953), p. 332.
5) A. J. Hegedüs, K. Sasvari and J. Neugebauer, *Z. anorg. u. allgem. Chem.*, **293**, 56 (1957).
6) K. Funaki and T. Segawa, *J. Electrochem. Soc. Japan (Nippon Denkikagaku Zasshi)*, **18**, 152 (1950).
7) E. Ya. Rode and V. N. Tverdokhlebov, *Zhur. Neorg. Khim.*, **3**, 2343 (1958).
8) J. H. Sturdivant, *J. Am. Chem. Soc.*, **59**, 630 (1937), cf. Ref. 3.
9) Y. Ahn, *J. Japan Soc. Powder Metallurgy (Funtai oyobi Funmatsu Yakin)*, **8**, 253 (1961).
* Heptamolybdate and octamolybdate are terms indicating chemical species, while dimolybdate and trimolybdate are terms indicating merely stoichiometry. Chemical formulae based on structural studies, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_4Mo_8O_{26}\cdot 4H_2O$, have been given for heptamolybdate and octamolybdate respectively.
10) Cf. Ref. 3.

powder patterns of the starting materials are given in Tables Ia, Ib and Ic. Table Ia is in good agreement with the data described in ASTM 11-71. There has been no description of other ammonium polymolybdates in ASTM.*

TABLE I

| (a) Ammonium heptamolybdate | | (b) Ammonium dimolybdate | | (c) Ammonium octamolybdate | |
|---|---|---|---|---|---|
| d Å | $I/I_1$ | d Å | $I/I_1$ | d Å | $I/I_1$ |
| 9.08 | 100 | 6.92 | 11 | 9.21 | 34 |
| 7.56 | 33 | 6.11 | 100 | 7.21 | 100 |
| 7.42 | 30 | 4.98 | 3 | 5.98 | 12 |
| 7.15 | 40 | 4.70 | 4 | 5.50 | 5 |
| 6.41 | 13 | 3.58 | 5 | 4.79 | 29 |
| 4.52 | 17 | 3.32 | 9 | 4.04 | 12 |
| 3.09 | 14 | 3.27 | 9 | 3.60 | 38 |
| 3.02 | 37 | 3.21 | 21 | 3.44 | 23 |
| 2.65 | 14 | 3.15 | 8 | 3.30 | 23 |
| 2.25 | 9 | 3.11 | 8 | 3.21 | 12 |
| 2.01 | 7 | 2.98 | 3 | 3.08 | 12 |
| | | 2.95 | 2 | 2.95 | 50 |
| | | 2.24 | 3 | 2.59 | 7 |
| | | 2.16 | 14 | 2.39 | 23 |
| | | | | 2.11 | 10 |

**The Determination of Evolved Ammonia.**—When a sample was heated in a furnace, the ammonia which evolved was carried into 1 N sulfuric acid by a stream of air and of nitrogen at 30 l./hr.; it was determined by titration using methyl orange as an indicator. By continually titrating it during the thermal decomposition, smooth curves of ammonia evolution were obtained, as Fig. 1 shows. The heating rate employed was 3°C/min.

**Thermogravimetric Measurement.**—Thermogravimetric measurement was performed in air at a heating rate of 3°C/min. by an automatic thermobalance.

**Analysis by an Omegatron Mass-spectrometer.**—Omegatron mass-spectrometric analysis was performed with about 30 mg. of a sample at $10^{-5}$ Torr, in the mass range between 1 and 50 and in the temperature range between room temperature and 400°C. The resolution of the omegatron was $M/\Delta M=56.5$ (calcd.) and 56.0 (obs.) at mass 28. It was possible to detect a partial pressure of $10^{-11}$ Torr by the omegatron. The measurement was performed at about every 50°C of elevation while the sample was being evacuated by oil diffusion pumps with an activated charcoal trap, the temperature being held constant during the measurement. Every time the sample was heated in a furnace, the pressure rose to $10^{-3}$ Torr at first because of the vigorous decomposition. However, since the omegatron measuremont was favorable at a pressure lower than $10^{-4}$ Torr, measurement was performed only when the pressure decreased to $10^{-5}$ Torr and became as constant as possible.

* By X-ray examination, the sample of ammonium trimolybdate was found to have changed into ammonium octamolybdate in about half a year when left undisturbed.

## Results

**The Evolution of Ammonia.**—It is important, in the pyrolysis study of ammonium salts, to determine continuously the ammonia which is liberated during the thermal decomposition. Figure 1 shows the ammonia evolution curves.

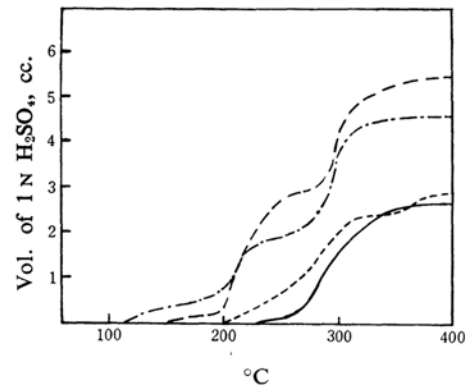


Fig. 1. Ammonia evolution curves.
– – – – Ammonium dimolybdate
—·—·— Ammonium heptamolybdate
——— Ammonium octamolybdate
- - - - - - - Ammonium trimolybdate

Heptamolybdate begins to evolve ammonia at the lowest temperature, about 120°C. Dimolybdate begins to evolve ammonia next, around 150°C; rapid evolution subsequently begins around 200°C. Octamolybdate and trimolybdate begin to evolve ammonia only above 200°C. By contrast, the evolution of ammonia is complete in all at almost the same temperature, 360~375°C. Each of the ammonia evolution curves of heptamolybdate and dimolybdate has three well-defined stages. X-Ray study illustrates that three different structures correspond to the respective stages, as will be discussed later.

**Weight-decrease Curves.** — Weight-decrease curves drawn by an automatic thermo-balance are shown by the solid lines in Figs. 3, 4, 5 and 6. It is noticeable that heptamolybdate and dimolybdate begin to decompose rapidly at 110 and 200°C respectively, their weight-decrease curves forming sharp inflections. Octamolybdate and trimolybdate, by contrast, decompose gradually at the beginning of heating. The end-points of decomposition are very clearly defined for all the molybdates. Decomposition is complete in all at almost the same temperature of 360~375°C. Heptamolybdate, dimolybdate and trimolybdate decompose in three stages, and octamolybdate in two stages.

**Observation by Means of an Omegatron Mass-spectrometer.**—Omegatron mass-spectrometer has been found to be effective in the

pyrolysis study in this research.[11] An example of the results obtained by the omegatron is given in Fig. 2. The observed mass numbers and the ionic species corresponding to them are as follows: 2 ($H_2^+$), 14($N^+$, $N_2^{2+}$, $CO^{2+}$), 15 ($NH^+$), 16 ($NH_2^+$), 17 ($NH_3^+$, $OH^+$), 18 ($H_2O^+$), 19 ($H_3O^+$), and 28 ($N_2^+$, $CO^+$).

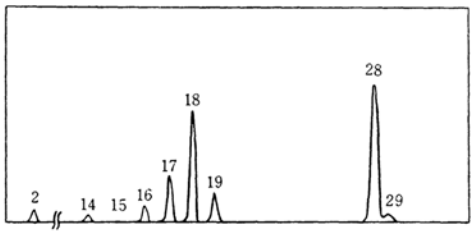


Fig. 2. Mass-spectrum of gases evolved from ammonium heptamolybdate at 395°C. Sensitivity of mass 2 is three times that of other masses.

Mass 29 seems to be a fragment of residual gas, but it is unidentifiable. The mass spectra were treated in the following way:

1) Since the observed intensities of the ionic current are proportional to the square root of the mass numbers, an appropriate adjustment was made.

2) Since one-fifth of $H_2O^+$(18) is known to appear as $OH^+$ in the same place as $NH_3^+$ (17) is observed, it was subtracted from the intensity of $NH_3^+$.

3) $NH^+$ and $NH_2^+$ are considered to be fractions of $NH_3^+$. These fractions, added to $NH_3^+$ (17) and then with one-fifth of $H_2O^+$ (18) subtracted, gave the sum of ammonia.

4) $H_3O^+$ (19), $OH^+$ (17) and $H_2O^+$ (18) gave the sum of water.

5) $N^+$ (14), $N_2^{2+}$ (14) and $N_2^+$ (28) gave the sum of nitrogen.*

6) The partial pressure of water, ammonia and nitrogen were calculated for each temperature and, for the sake of comparison, were re-estimated as values at the same total pressure. Thus Fig. 7 was obtained.

The final product obtained in the omegatron at $10^{-6}$ Torr and at 400°C consisted of purple-black oxides of molybdenum, in which $MoO_3$, $Mo_9O_{26}$ and $Mo_4O_{11}$ are predominant and $Mo_8O_{23}$ is only auxiliary.

## Discussion

Since one molecule of water accompanies every two molecules of ammonia when they are liberated from the salt, the ammonia evolution curves, $NH_3$ curves, shown in Fig. 1, must be represented as $(NH_4)_2O$ curves. By superimposing the latter on the weight-decrease curves obtained by the automatic thermo-balance, the dotted lines in Figs. 3, 4, 5 and 6 are obtained. With ammonium heptamolybdate tetrahydrate (Fig. 3), a fairly good coincidence as to the shape and height of the curves between 130 and 360°C is noticeable. The three stages in the $(NH_4)_2O$ curve correspond to those in the weight-decrease curve. Therefore, the weight decrease from 130°C up to 360°C may be correlated with the evolution of ammonia and water accompanying it. Consequently, the weight decrease from room temperature up to 130°C is correlated with the dehydration of crystals. The theoretical value of four molecules of the water of hydration is shown by an arrow mark; it is in good agreement with the observed value. We might conclude that dehydration begins very slowly at room temperature, that around 115°C dehydration becomes rapid, and that it is almost complete at 130°C. The discrepancy between the weight-decrease curve and the $(NH_4)_2O$ curve above 360°C is due to the formation of nitrogen from ammonia, which will be discussed below. Indeed, the observed values of the quantitative determination of ammonia always fall short of the theoretical values.

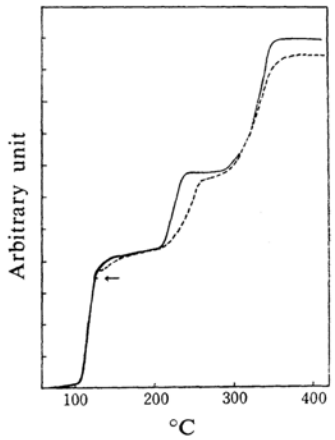


Fig. 3. Weight-decrease curve (solid line) and $(NH_4)_2O$ curve (dotted line) of ammonium heptamolybdate.

The four molecules of water of hydration are not included in the crystal structure of the discrete heptamolybdate ion, $Mo_7O_{24}^{6-}$.[12] The crystal structure of heptamolybdate does not break down until 130°C, when most of

11) M. Onchi and E. Ma, *J. Phys. Chem.*, 67, 2240 (1963).

* $CO^+$ (28) and $CO^{2+}$ (14) as background are evacuated to negligible amounts, Moreover, the pattern coefficient of the 28 peak justifies its identification as nitrogen.

12) Cf. Ref. 3.

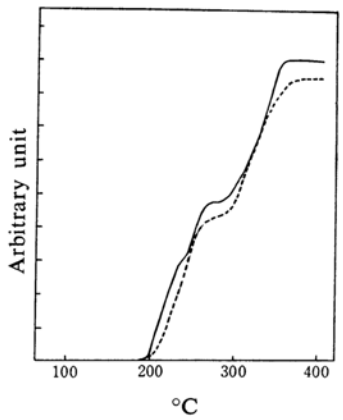


Fig. 4. Weight-decrease curve (solid line) and $(NH_4)_2O$ curve (dotted line) of ammonium dimolybdate.

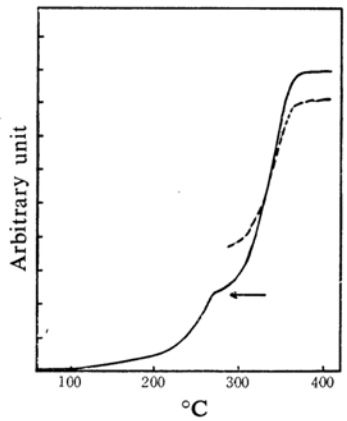


Fig. 5. Weight-decrease curve (solid line) and $(NH_4)_2O$ curve (dotted line) of ammonium octamolybdate.

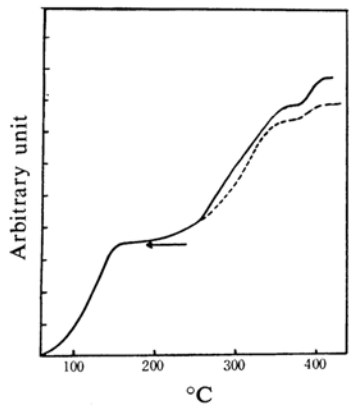


Fig. 6. Weight-decrease curve (solid line) and $(NH_4)_2O$ curve (dotted line) of ammonium trimolybdate.

the water is lost. As the dehydration does not proceed step by step, some part of the water may be regarded as of the zeolitic type.

Since ammonium dimolybdate is not hydrated, the weight-decrease curve is approximately equal to the $(NH_4)_2O$ curve, and the decomposition begins at a temperature higher than that in the case of heptamolybdate. (Fig. 4).

In the case of trimolybdate, dehydration is complete around 150°C, and the crystal structure changes into octamolybdate above 200°C.

In the case of ammonium octamolybdate dihydrate, dehydration is complete around 280°C, and the crystal structure of octamolybdate does not break down until around 360°C. Therefore, some of the water molecules are tenaciously held up to 280°C. Consequently, they must be water molecules of a different type. (Figs. 5 and 6).

The step-by-step decompositions indicate that water and ammonia, presumably as ammonium ions in the crystal, are bonded with the molybdate ions in different strengths, and that there should be a further difference in bonding strength in ammonia. To each stage of the weight-decrease curves, there should be a corresponding crystal structure. Studies of structural change will be reported on in a succeeding paper.

The ultimate discrepancy between the weight-decrease curves and the $(NH_4)_2O$ curves in Figs. 3, 4, 5 and 6 may be assumed to be referrable to the formation of nitrogen from ammonia, as has been mentioned above. In order to confirm this, the process of the thermal decomposition was analyzed by means of omegatron, taking ammonium heptamolybdate as an example.

The most significant information provided by the omegatron was that the existence of nitrogen in the process of thermal decomposition was definitely established. Water, ammonia and nitrogen are plotted on the ordinate of the same arbitrary unit in Fig. 7, which, therefore, provides an estimate of the relative values of these gases. The sudden decrease in

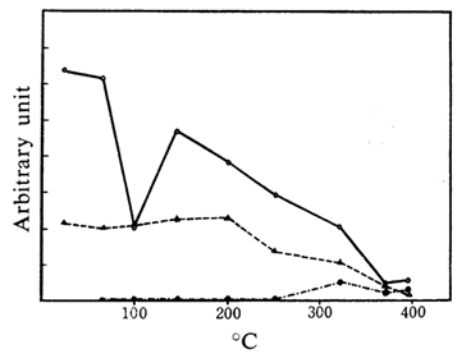


Fig. 7. Partial pressure vs. temperature
—— Water ---- Ammonia
—·—·— Nitrogen

water quantity at 100°C might be due to the end of dehydration. Nitrogen formation began around 250°C and reached a maximum around 320°C. Consequently, it became of interest to determine whether hydrogen also existed. Molecular hydrogen was also successfully detected by the omegatron. The formation of hydrogen goes on in a way quite similar to that of nitrogen, i. e., beginning to form around 250°C and reaching a maximum around 320°C. The hydrogen is not to be considered to come from water. In Fig. 8 the amounts of nitrogen and hydrogen are plotted on ordinates of different arbitrary units. Neither $H_2O^+$ nor $H_3O^+$ has a tendency to increase when nitrogen is being yielded.

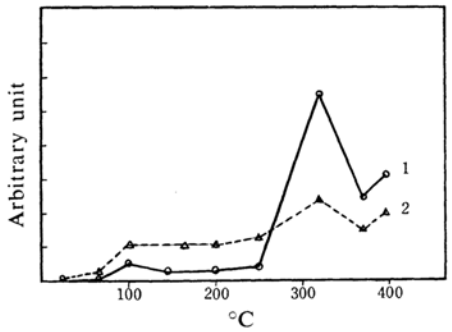


Fig. 8. Partial pressure vs. temperature.
1) Nitrogen 2) Hydrogen

These findings might be interpreted as meaning that ammonia is oxidized to nitrogen by the molybdenum oxide resulting from the thermal decomposition. Thus the molybdenum oxide is reduced to a lower oxide. An alternative interpretation is that ammonia is decomposed into nitrogen and hydrogen at the surface of molybdenum oxide through its catalytic action. The detection of hydrogen by the omegatron may support the latter interpretation. The amount of nitrogen at 320°C is more than ten times the amount at 250°C, while the amount of hydrogen at 320°C is less than ten times that at 250°C. Therefore, a larger amount of nitrogen must be yielded through oxidation than through decomposition. The formation of nitrogen from ammonia was detected in vacuo by the omegatron. Similar considerations apply to the formation of nitrogen from ammonia in air. It takes place even more vigorously if it is yielded through oxidation. Since the precise mole ratios of the nitrogen and hydrogen formed in vacuo have not yet been determined, quantitative argument will be deferred pending further investigation.

Figure 7 shows that water is evolved more abundantly than ammonia throughout the process; this is contrary to the theoretical expectation, and the cause is not certain. One possible explanation is as follows: When the sample was heated in a furnace while being evacuated, it decomposed vigorously at first and the pressure rose to $10^{-3}$ Torr. The omegatron measurement was performed, however, only when the pressure decreased to $10^{-5}$ Torr, when the evolution of the gases was almost in equilibrium. Accordingly, the composition of evolving gases might be different from that at $10^{-3}$ Torr.

## Summary

The thermal decomposition of ammonium di-, hepta-, tri- and octa-molybdate has been investigated by means of thermogravimetric analysis, ammonia determination and the use of an omegatron mass-spectrometer. Both weight-decrease curves and ammonia evolution curves exhibit stepwise decomposition, indicating that there should be a difference in bonding strengths of water and of ammonia, presumably as ammonium ions in the crystal, with molybdate ions. Hepta-, di- and trimolybdate decompose in three stages, and octamolybdate in two stages. A certain crystal structure should correspond to each stage. Dehydration precedes deammoniation. Dehydration is complete at about 130, 150 and 280°C with hepta-, tri- and octa-molybdate respectively. Deammoniation is complete in all at the same temperature of 360~375°C. The existence of nitrogen above 250°C in vacuo has been established. Nitrogen is yielded in the process of the thermal decomposition through oxidation as well as through the catalytic decomposition of ammonia. Nitrogen reached a maximum around 320°C. As evidence for the formation of nitrogen through decomposition, hydrogen was also detected above 250°C, and was found to reach a maximum at about 320°C, although in a much smaller quantity.

The author wishes to express his deep gratitude to Professor Kumasaburo Kodera and to Professor Sukeji Kachi of Kyoto University for their continued interest in this investigation and for their valuable suggestions. He is also greatly indebted to Dr. Minoru Ozasa of the Matsushita Electronics Corporation for courtesies extented to him and for fruitful discussions. He wishes to thank Dr. Masaru Onchi of Kyoto University for measurement using the omegatron mass-spectrometer.

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