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Thermal Decomposition of Ammonium Salts of Transition Metal Oxyacids. II. The Determination of the Gas Constituents Evolved by Ammonium Paramolybdate Decomposition

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Gases evolved by the decomposition of ammonium paramolybdate tetrahydrate have been analyzed by means of an omegatron mass spectrometer. Only water molecules of the hydration were eliminated during the first stage of decomposition, and the final stage was not the elimination reaction of ammonia but the oxidation reaction of ammonia by Mo(VI) oxide. Between 150 and 250°C, ammonia and water were evolved in a mole ratio of roughly 2:1, corresponding to the elimination of $(NH_4)_2O$. However, the range is not clear because of the overlap of the elimination of water at the lower limit and that of nitrogen at the upper limit. At higher temperatures, a small amount of NO was observed.

In a previous paper[1)] it was described that ammonium paramolybdate tetrahydrate (APM) is decomposed in four stages under 760 Torr and in five stages under below 130 Torr; those results were based on thermogravimetric analyses.

Many published papers have discussed the gases evolved in each stage of decomposition simply on basis of the thermogravimetric analysis curves (TGA curves). It is said that in the first stage, ammonia and water are simultaneously removed as soon as four molecules of water are removed, and no separate stages have been observed in this process. The mole ratio of ammonia to water is 2:1; it corresponds to that of $(NH_4)_2O$. The second and the third decomposition stage are also considered to be the elimination of $(NH_4)_2O$ as ammonia and water.

Ma[2)] carried out the analysis of evolved gases by means of an omegatron mass spectrometer and found that nitrogen began to come out around 250°C and reached a maximum around 320°C. He also found that hydrogen was evolved along with the nitrogen; he concluded that both were produced by the decomposition of ammonia on the surface of Mo(VI) oxide. He also measured the amount of evolved ammonia by chemical analysis and found a general agreement with the weight loss. He pointed out that any discrepancy is due to the formation of nitrogen from ammonia. In addition, he reported that water is evolved more than would be theoretically expected from the amount of ammonia. Therefore, it was considered worth while to study the gas evolution by thermal decomposition. Especially, the evolution of nitrogen observed by Ma and the dehydration stage described in the previous paper was confirmed by gas analysis. The present studies were carried out by means of an omegatron mass spectrometer.

Experimental

Apparatus and Procedure. Figure 1 shows a schematic diagram of the apparatus; it was constructed of molybdenum glass and was composed of a fused silica reaction tube coupled with a pressure-measuring device, an omegatron mass spectrometer, and two evacuating systems. The apparatus was bakable at 450°C, and its ultimate vacuum was 1×10^{-8} Torr. The main residual gas was carbon monoxide, accompanied by small amounts of carbon dioxide and water. Between the reaction tube and the omegatron, there was a copper seal metal valve and a capillary leak which reduced the pressure in the reaction tube to below 1×10^{-5} Torr for the operation of the omegatron. A McLeod gauge was used to measure the pressure of the noncondensable gases, while the total pressure of the omegatron system was measured by means of a Bayard-Alpert gauge. The evolving gases were analyzed by means of the omegatron mass spectrometer. The omegatron tube was of Mitsubishi Electric make, simple box type, and was placed in a magnetic field of 4500 gauss. The resonance ion current of the omegatron was measured by means of a Takeda TR-84H vibrating reed electrometer. The temperature of decomposition was measured by means of a chromel-alumel thermocouple.

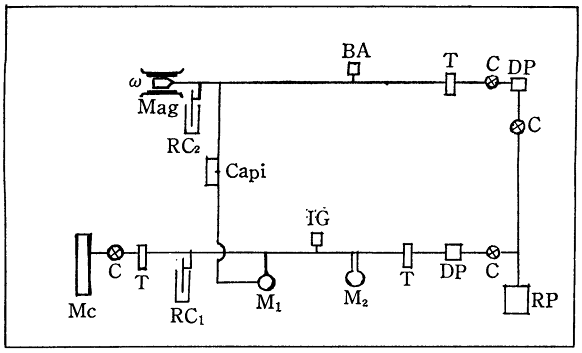

Fig. 1. Apparatus for gas analysis by omegatron.
RP: Rotary pump
DP: Oil diff. pump
C: Grease cock
T: Liq. N_2 trap
M_1 M_2: Metal valve
BA: BA gauge
IG: Ionization gauge
RC: React. cell
Capi: Capillary
ω: Omegatron
Mag: Magnet
Mc: McLeod gauge

Measurement of the Evolving Gases. The gases evolved in each decomposition stage were analyzed in the closed system and in the evacuating system. A powdered sample of Merck extra pure grade (50 mg) was placed in the decomposition cell, RC_1, in the case of the closed system. The measurement of the evolved gases was carried out from room temperature (20°C) to 500°C at intervals of 50°C. Usually, after about one hour the pressure of the evolved gases attained a stationary value. Then the gases were

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1) I. H. Park, This Bulletin, **45**, 2739 (1972).

2) E. Ma, *ibid.*, **37**, 171 (1964).

Table 1. Pattern coefficients of various gases

Gases	Mass									
	12	14	15	16	17	18	19	28	32	44
NH_3		1.2	4.2	7.0	100					
H_2O				1.8	21	100	10			
N_2		10						100		
CO	4—5	0.3-0.4		4				100		
CO_2	2			7					0.3	100

introduced into the omegatron through the capillary leak and were analyzed. After the measurements, the remaining gases were evacuated through a metal valve, M_2. After the pressure of the reaction system has attained 1×10^{-5} Torr, the constituents of the residual gases were checked. Then, the temperature of the cell was raised to the next decomposition temperature and the gases evolved were analyzed. The same procedure was repeated up to 500°C.

The observed intensities of the different gas ions were compared in the following way. At pressures lower than 10^{-5} Torr, the relationship of the ion current to the pressure may be represented by the following equation:

$$S \cdot P = i_+ / i_-$$

where S is the sensitivity and can be treated much as the sensitivity in the ionization gauge, i_+, the ionic current produced by the electron current, i_-, and P, the pressure. The values of the sensitivity ratio for the ionization gauge for various gases determined by Wagener and Johnson[3] were used in estimating the relative amounts of N_2, H_2O, and CO_2. For the other gases, the relative sensitivities were estimated on the assumption that the sensitivity of the ionization gauge, S, and N_e, the total number of electrons per gas molecule, have a linear relationship.[4] Therefore, for the most important gases, NH_3 and H_2O, the sensitivities are nearly equal. The difference in the conductance of the gas should be considered in exact measurements, but as it is proportional to the square root of the molecular weight and as the main gases measured were ammonia and water, the correction is omitted here.

For the identification of the spectrum, the pattern coefficients of the relevant gases were determined to be as is shown in Table 1. They are in good agreement with Klopfer's[5] results. Hydrocarbons from the greased stop cock which connects the reaction system to the McLeod gauge might cause some trouble in the measurement; for instance, they might react with the sample. Therefore, to confirm whether or not there was any effect, another experiment was carried out by using an evacuating system free from grease vapor. This was carried out below 10^{-6} Torr under continuous evacuation. For this purpose, the sample cell, RC_2, near the omegatron was used. This procedure was carried out in order especially to investigate the gas constituents above 250°C.

Dehydration Process. The measurements were carried out in a closed system under an ambient pressure of 10^{-1} Torr in order to check the elimination of the hydrated molecules prior to the evolution of ammonia, under a low temperature as far as was possible. The evolved gases were measured at intervals of 10°C from room temperature to 100°C.

Oxidation of Ammonia by Molybdenum Oxide. Molybdenum oxides, obtained by the thermal decomposition of APM heated up to 450°C under 760 Torr and under 10^{-3} Torr, were used. The oxide sample was placed in RC_1 and was heated under 10^{-1} Torr ammonia. The gases produced by the reaction for 1 hr were investigated by means of the omegatron at intervals of 50°C from 300 to 500°C. Of course, the evolution of ammonia or nitrogen from the sample itself has previously been examined, but no ammonia or nitrogen was detected.

Results and Discussion

The relative amounts of the gases evolved by thermal decomposition in a closed system are shown in Fig. 2 as a function of the temperature. The mass spectra before and after the production of nitrogen, namely, at 250, 300, and 350°C, are shown in Fig. 3. Gas analysis was carried out at the temperature near the maximum of dw/dt on the DTG curve given in the previous paper. As was reported in that paper, it was assumed, from the results of TGA, that there was a dehydration process under pressures lower than 130 Torr, but its existence should be confirmed by gas analysis. Only Funaki[6] has pointed out the existence of the dehydration process of four molecules of water at 110°C. On the other hand, from the titration of

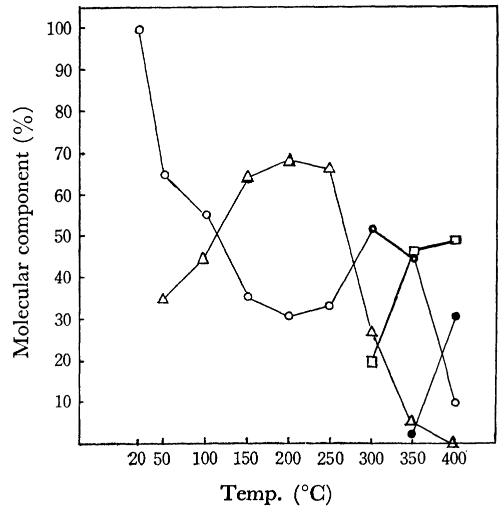

Fig. 2. Molecular component of decomposed gases.
○: H_2O △: NH_3 □: N_2 ●: CO_2

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[3] S. Wagener and C. B. Johnson, *J. Sci. Instr.*, **28**, 278 (1951).

[4] Dushman-Lafferty, "Scientific Foundation of Vacuum Technique," 2nd edition, John Wiley & Sons Inc., (1962), p. 326.

[5] A. Klopfer, S. Gorbe, and W. Schmidt, *Vacuum Symposium Transaction*, **27**, (1960).

[6] K. Funaki and Segawa, *J. Electrochem. Soc. Jap.*, **18**, 152 (1950).

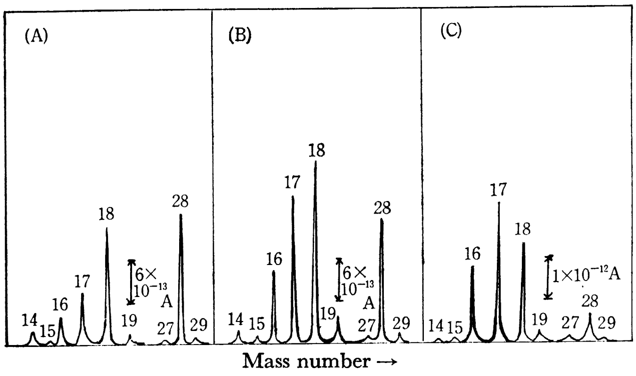

Fig. 3. Mass spectra of the evolved gases at 250—350°C.
(A): 350°C, $P=6.1\times10^{-7}$ Torr, $I_e=1.0\ \mu A$, $V_{rf}=0.7\ V_{rms}$
(B): 300°C, $P=9\times10^{-7}$ Torr, $I_e=1.0\ \mu A$, $V_{rf}=0.7\ V_{rms}$
(C): 250°C, $P=1\times10^{-6}$ Torr, $I_e=1.0\ \mu A$, $V_{rf}=0.7\ V_{rms}$

evolved ammonia, Ma presumed the existence of a dehydration process just before the removal of $(NH_4)_2O$ within the first stage of the decomposition under 760 Torr. In his thermogram, however, the separation of the two processes is not seen. Also, by the present experiment, the separate dehydration process was not observed in the first decomposition process under 760 Torr. Figure 4 shows the limit of dehydration, *i.e.*, the beginning of ammonia evolution in an ambient pressure of 10^{-1} Torr. Under 10^{-1} Torr and below 70°C the peak of $m/e=17$ is considered to be almost entirely the fragment ion of H_2O, and the amount of ammonia is very small. However, at 80°C about one third of the peak may be attributed to ammonia. Therefore, the evolution of ammonia, *i.e.*, the removal of $(NH_4)_2O$, began at about 80°C; below this temperature only water of hydration was released. Thus, the existence of the dehydration stage under 10^{-1} Torr was confirmed. In Table 2, the temperatures at which ammonia began to be released in different ambient pressures are shown. From Table 2, it is clear that the temperature of ammonia production shifts to higher temperatures as the ambient pressure increases and that a part of the water molecules of hydration are removed at the beginning of decomposition, but the removal of the residual water overlaps with that of ammonia. The higher the pressure, the greater is the overlapping of the two procedures. Ammonia exists in the crystal as ammonium ions, and it is released with the water in the composition of $(NH_4)_2O$. Generally, it has been considered that the final product, MoO_3, is produced by the removal of only NH_3 and H_2O, although the analysis of the evolved gas has not been done. Ma analyzed the evolved gases for the first time and found out that, in the stage of the removal of $(NH_4)_2O$, the ratio of NH_3 and H_2O was not 2: 1. However, in the present study, it may be seen in Fig. 2 that the ratio of 2: 1 continued from 150 to 250°C; it is considered that this corresponds to the elimination of $(NH_4)_2O$. It was found by the thermogravimetric analysis that the intermediate obtained by the decomposition at this stage has the composition of $(NH_4)_2O\cdot4MoO_3$; it is an extremely stable compound. The TGA curve shows that this stable compound decomposes above 250°C. According to Figs. 2 and 3, the evolution of ammonia decreased suddenly at 300°C; simultaneously, the peak of $m/e=28$ appeared. This is clearly the peak of nitrogen. It may be seen from Table 3 that the pressure at 300°C measured by the McLeod gauge without a cold trap was below 1/10 of that at 250°C. The value of the total pressure is not very reliable because of the pressure of the condensable water vapor; nevertheless, it is true that the amounts of gases evolved are very small at this temperature.

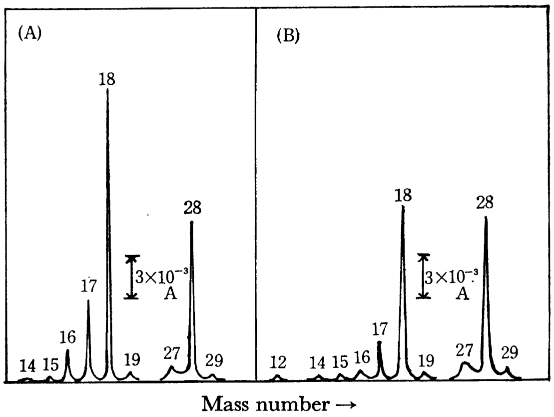

Fig. 4. Mass spectra of the evolved gases at 70 and 80°C.
(A): 80°C, $P=7\times10^{-7}$ Torr, $I_e=0.5\ \mu A$, $V_{rf}=0.9\ V_{rms}$
(B): 70°C, $P=7.3\times10^{-7}$ Torr, $I_e=0.5\ \mu A$, $V_{rf}=0.9\ V_{rms}$

The total pressure of gas evolved at 350°C again increased to twice that at 300°C and reached a maximum. Hydrogen was not observed at all; the main products at this stage were water and nitrogen, which

TABLE 2. VARIATION OF DEHYDRATION TEMPERATURE IN VARIOUS AMBIENT PRESSURE OF DECOMPOSITION

Ambient pressure (Torr)	760	130	70	20	5	10^{-1}	10^{-3}	10^{-5}
Temperature which NH_3 evolution begins	115[a)]	105[b)]	95[b)]	85[b)]	80[b)]	80[c)]	70[b)]	50[c)]

a) temperature proposed by Ma. b) temperature of $dw/dt=$min. in 1st decomposition process on Figs. 6 and 7 in previous paper. c) temperature determined by omegatron.

TABLE 3. TOTAL PRESSURE OF EVOLVED GASES

Temperature (°C)	20	50	100	150	200	250	300	350	400
Pressure ($\times10^{-1}$ Torr)	0.26	1.13	4.8	6.8	11.9	10.6	1.3	2.5	0.41

was the oxidation product of ammonia with Mo(VI) oxide. However, the amount of water is considerably less than that which should be produced by the oxidation of ammonia. This discrepancy may be explained by the loss of water by adsorption on the inside wall of the glass apparatus, because the total amount of gas evolved was rather small.

The gases evolved at 400°C were mainly nitrogen and carbon dioxide of $m/e=44$, and no ammonia was observed. As the total pressure was very low at this temperature, the amounts of nitrogen and water were very small. Therefore, the thermal decomposition of APM was completed here. The carbon dioxide might be produced by the oxidation of the impurity carbon contained in the sample, or part of it might come from the grease vapor. As for the production of carbon dioxide, Onchi and Kusunoki[7] have reported that, by the thermal decomposition of MoO_3 *in vacuo*, the main gaseous product about 400°C was carbon dioxide, the production of oxygen-deficient oxide is attributable to the reduction by the impurity. The main gases observed at 450 and 500°C were carbon dioxide and carbon monoxide, plus a small amount of NO, $m/e=30$. Nitric oxide might be produced by the further oxidation of ammonia. Oxygen with $m/e=32$ has not observed throughout the decomposition up to 500°C.

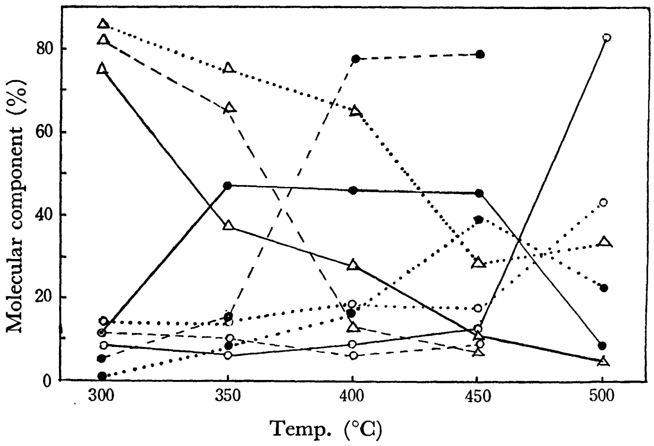

Fig. 5. Molecular component of N_2, H_2O, and NH_3, evolved by reaction of NH_3 with MoO_3.

—— - - - }MoO_3 prepared in vac.

······ MoO_3 prepared in air

●: N_2, ○: H_2O, △: NH_3

The experiment in the evacuating system confirmed that the evolution of ammonia, water, and nitrogen was similar to that in the closed system except that the temperature of nitrogen production was shifted to a slightly higher temperature. This fact suggests that the oxidation of ammonia takes place at the moment of its production, or that the collisions with the surface need not be repeated many times, though the produced NH_3 comes in contact with the oxide surface. The results of the oxidation of ammonia by the MoO_3 produced by the thermal decomposition of APM in air or *in vacuo* show that nitrogen was formed about 300°C and that the amount reached its maximum at 350—400°C for both samples (Fig. 5). The tendency of the reaction is similar to the case of APM but the temperature seems to be shifted to a higher value. However, no detailed discussion can be made because of the lack of reproducibility of the data. It was found that the evolution of H_2O came later than the production of N_2. The reason for this may be as follows: when NH_3 was oxidized on the surface of MoO_3, the O–H bond was perhaps produced in a crystal by binding the H of NH_3 and the O of MoO_3, and later, as the temperature rose, this O–H was perhaps eliminated by way of the formation of H_2O. Further examinations are needed to confirm this conclusion on the basis of the reproducibility of the experimental results. Nevertheless, it was proved that the ammonia produced in a crystal is actively oxidized to nitrogen on the surface of MoO_3 or on the interface of the crystal.

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[7] M. Onchi and I. Kusunoki, *Nippon Kagaku Zasshi*, **85**, 612 (1964).