Thermal Decompsition of Ammonium Salts of Transition Metal Oxyacids. IV.[1] Determination of Constituents of Gases Evolved in Decomposition of Ammonium Chromate

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Constituents of gases evolved in thermal decomposition of ammonium chromate and ammonium dichromate have been studied by an omegatron mass spectrometer. From the data of gas analysis, the following conclusions have been obtained. The decomposition of the first step started with proton transfer mechanism and the ratio of NH_3 to H_2O was not 2: 1 at the beginning. The second step corresponded to the formation of N_2, N_2O, and H_2O through oxidation of NH_3 by the chromate anion. The decomposition in the third step was accompanied by the evolution of oxygen molecules. The production of CrO_3 was confirmed by comparing the dissociation pressure of CrO_3 produced in AC decomposition with that of pure CrO_3. The decomposition in the last step corresponded to the process from CrO_2 to Cr_2O_3, with the evolution of O_2, CO_2, and CO.

In the preceding work,[1] the thermograms of ammonium chromate (AC) and ammonium dichromate (ADC) were obtained, and the composition and structure of each intermediate were determined from the results of weight decrease data and X-ray analysis.

The evolved gases in the decomposition of AC have not yet been analyzed but only the gases evolved in ADC decomposition near 200°C have been studied by some investigators. For instance, Simpson *et al.*[2] have reported that N_2, N_2O, and H_2O were the main products in the range of temperature from 180 to 215°C. However, the gas constituents reported by other workers differed from those mentioned above. In this study the evolved gases in the thermal decomposition of AC and ADC by heating them from room temperature up to 500°C were analysed by an omegatron mass spectrometer, in the hope of better interpretation of the thermogram and better understanding of the mechanism of decomposition in each step.

Experimental

Apparatus and procedure for gas analysis were similar to those used in the previous work,[3] except the use of dry ice to remove the hydrocarbon vapor from the stopcock grease. The total pressure was measured by a Pirani gauge. Extra pure reagents of AC and ADC from Nakarai Chemical Co. were used without further purification. Samples used were both powder and crystal grain. The gas analysis was carried out in closed and in evacuating systems up to 500°C, with the intervals of 50°C. The gaseous products were identified by the omegatron, comparing the mass spectrum observed with the standard pattern obtained from pure gases. In addition to the patterns for N_2, H_2O, CO, and CO_2 described in the previous paper,[3] the pattern coefficients for N_2O and O_2 are shown in Table 1.

Table 1. PATTERN COEFFICIENTS OF OXYGEN AND NITROUS OXIDE

Gas	Mass No.						
	14	15	16	28	30	32	44
O_2			10—15			100	
N_2O	6	2—3	3	30—45	25—30		100

The decomposition pressure of CrO_3 was measured by similar method to that of Kodera *et al.*[4] Samples of CrO_3 used were either CrO_3 sample prepared in the laboratory or commercially available CrO_3 (extra pure reagent of Nakarai Chemical Co.). The former was prepared by heating AC up to 240°C and keeping it for 20 hr at this temperature during annealing. Color of the product was dark brown. The temperature range of measurement was from 225 to 400°C, and the decomposition of CrO_3 to CrO_2 proceeded at this temperature range.

Results

The Gases Evolved in the Closed System and in Evacuating System. The decomposed gases from AC at room temperature were studied in a closed system. The gases were collected for one hour and used for mass spectrum determination. After the measurement, the system was evacuated again and the same procedure was repeated at the interval of one hour. Percentages of NH_3 and H_2O were determined, as shown in Table 2. Similarly the constituents of decomposed gases from

Table 2. PERCENT MOLAR FRACTIONS OF THE DECOMPOSED GASES AT 25°C (AC)

Run	1	2	3
Total pressure (Torr)	8.4×10^{-2}	6.7×10^{-2}	8.5×10^{-2}
H_2O	15	25	28
NH_3	84	74	72

ADC at 200°C were studied in the closed system at the interval of 30 min. The percentages of NH_3, oxidation products of NH_3 and H_2O, were determined, as shown in Table 3. Percent molar fractions of the evolved gases in the decomposition of AC and ADC at various temperatures are plotted in Figs. 1 and 2,

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1) Part III: I. H. Park, This Bulletin, **45**, 2749 (1972).

2) J. Simpson, D. Taylor, and D. M. W. Anderson, *J. Chem. Soc.*, **1958**, 2378.

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

4) K. Kodera, I. Kusunoki, and S. Schimidzu, This Bulletin, **41**, 1039 (1968).

respectively. Similar measurements were carried out in an evacuating system using both crystal grain and powder. Evacuating system was constructed by placing the reaction tube near omegatron. The results obtained for AC under various conditions are shown in Figs. 3(a) and 3(b).

Measurement of Dissociation Pressure of CrO_3. The mass spectra were observed at various temperatures, starting from 225°C, for the CrO_3 sample prepared in the laboratory. Constituents of gas evolved were CO_2 with trace of nitrogen compounds. The mass spectrum of gas evolved at 300°C is shown in Fig. 4(a). The peak for m/e=44 is mainly due to CO_2^+ (95%) rather than N_2O^+ (5%). The peak for m/e=28 is assumed to be due to CO^+ or N_2^+, but from the pattern coefficient[3] it was decided that the peak is due to CO^+.

TABLE 3. PERCENT MOLAR FRACTIONS OF THE DECOMPOSED GASES AT 200°C (ADC)

Run	1	2	3	4	5
Total pressure (Torr)	2.9×10^{-1}	1.4×10^{-1}	1.2×10^{-1}	1.3×10^{-1}	9.5×10^{-2}
N_2O	35.3	38.3	51.2	62.7	59.0
N_2	53.6	54.1	33.3	33.7	12.0
H_2O	7.6	5.9	9.3	3.6	17.0
NH_3	3.5	1.8	—	—	—

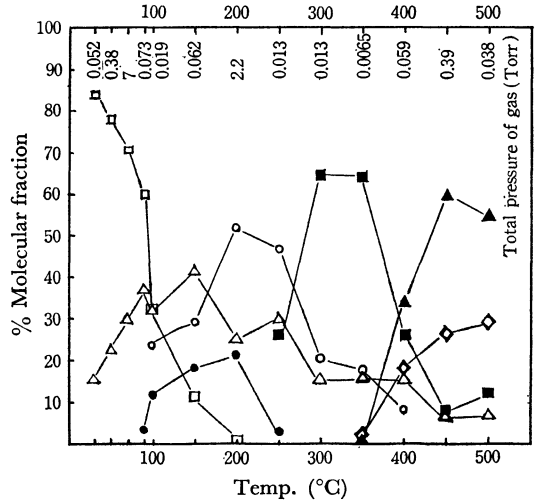


Fig. 1. Percent molecular fraction of the gases evolved by AC decomposition.
□ NH_3, △ H_2O, ● N_2, ○ N_2O, ■ CO_2, ◇ CO, ▲ O_2

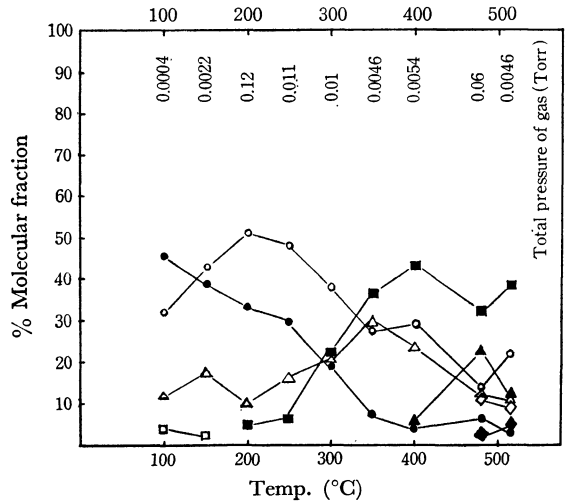


Fig. 2. Percent molecular fraction of the gases evolved by ADC decomposition.
□ NH_3, △ H_2O, ● N_2, ○ N_2O, ■ CO_2, ◇ CO, ▲ O_2, ◆ NO

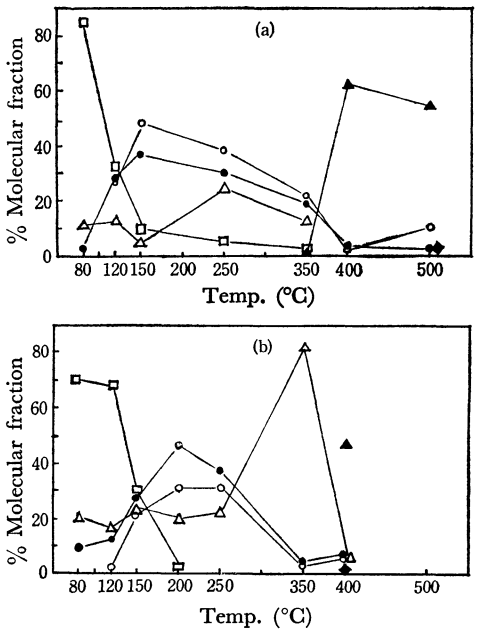
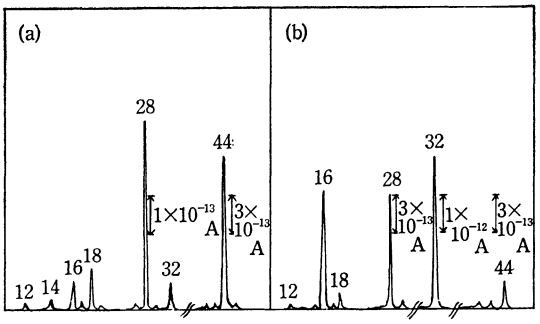


Fig. 3. Percent molecular fraction of the decomposed gases from AC in evacuating system.
(a) powder (b) whole crystal grain
□ NH_3, △ H_2O, ● N_2, ○ N_2O, ▲ O_2, ◆ NO



→ Mass number

Fig. 4. Mass spectra of the gases which evolved from the prepared CrO_3.
(a): 300°C, $P_{total}=1.6\times10^{-7}$ Torr $P_{gas}=2.8\times10^{-3}$ Torr
(b): 375°C, $P_{total}=1.2\times10^{-6}$ Torr $P_{gas}=5.6\times10^{-2}$ Torr

TABLE 4. TOTAL PRESSURE AND PARTIAL PRESSURE OF THE GASES EVOLVED BY PURE CrO_3 DECOMPOSITION

Temp., (°C)	Total press. at equil. (Torr)	m/e= 44	m/e= 32	m/e= 28	Partial press. of O_2 (Torr)
325	1.6×10^{-3}	69.5	7.1	23.5	1.1×10^{-4}
350	1.6×10^{-3}	47.8	21.3	30.7	3.4×10^{-4}
375	3.0×10^{-3}	17.1	39.8	43.3	1.2×10^{-3}
400	8.5×10^{-3}	12.9	72.5	14.6	6.2×10^{-3}
425	1.4×10^{-2}	10.1	78.3	11.6	1.1×10^{-2}
450	1.9×10^{-2}	9.9	79.2	10.9	1.5×10^{-2}

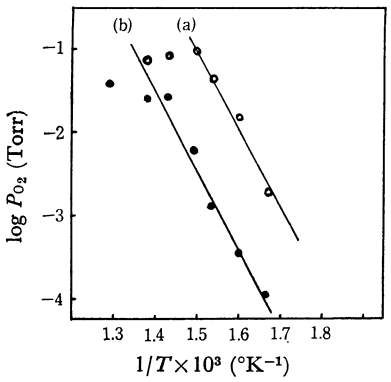


Fig. 5. Dissociation pressure of the prepared CrO_3 (a) and standard CrO_3 (b).

Oxygen is seen at $m/e=32$. The fact that CO_2 is formed is in agreement with the results of Kodera *et al.*[4] on the thermal decomposition of metal oxides *in vacuo*. Below 300°C, oxygen molecules produced might be consumed for the oxidation of nitrogen compounds or carbon impurities. The mass spectrum of gas evolved at 375°C is shown in Fig. 4(b). Main product is O_2 with some amounts of CO and a small amount of CO_2.

For comparison, similar experiments were carried out with the pure CrO_3[5] sample above 325°C. The results are shown in Table 4. The dissociation pressures of the prepared CrO_3 and pure CrO_3 were plotted against $1/T$ in Fig. 5.

Discussion

First Decomposition Step. From the results of thermogravimetric analysis,[1] it was supposed that AC was decomposed to ADC at the first step, two molecules of NH_3 and one molecule of H_2O being eliminated at this step. However, according to the gas analysis by omegatron, as seen in Fig. 1 and Table 2, the theoretical ratio 2: 1 (=NH_3: H_2O) in the gaseous phase does not appear until it is heated up to about 90°C, but this ratio is much larger than 2: 1 below 90°C. Namely, the evolution of NH_3 and H_2O does not take place in the form of $(NH_4)_2O$ as in the case of the decomposition of ammonium paramolybdate described in the previous paper,[3] where the ratio of NH_3 to H_2O was always 2: 1. Accordingly, it is considered that the elimination mechanisms of NH_3 and H_2O in the decomposition of ammonium chromate and ammonium paramolybdate differ with each other. Table 2 suggests that NH_3 is eliminated rapidly in the beginning whereas the amount of H_2O evolving gradually increases as the reaction proceeds. In other words, NH_3 is eliminated before H_2O is formed from the crystal in this step, and the following decomposition does not proceed: $2(NH_4)_2CrO_4 \longrightarrow (NH_4)_2Cr_2O_7+2NH_3+H_2O$.

5) This sample was sublimated at 200°C *in vacuo* and was condensed as dark red crystals at the upper part of the reaction cell, while CO_2 gas evolved. The dissociation pressure of CrO_3 at 650°C was 1.3×10^{-3} Torr and green Cr_2O_3 was condensed at the upper part of the reaction cell while the pressure decreases rapidly.

As described by Davies *et al.*[6] on the thermal decomposition of ammonium perchlorate, it is considered that only NH_3 is eliminated at the first step from the crystal by proton transfer mechanism. Thus, the mechanism may be expressed by

$$2(NH_4^+\text{-}CrO_4^{2-}) \rightleftharpoons 2(NH_3\text{-}H\text{-}CrO_4^-) \rightleftharpoons 2(NH_3\text{-}HCrO_4^-)$$
$$\quad\;\; | \qquad\qquad\quad | \qquad\qquad\quad |$$
$$\quad NH_4^+ \qquad\quad NH_4^+ \qquad\quad NH_4^+$$
$$\quad (I) \qquad\qquad (II) \qquad\qquad \Downarrow$$
$$2NH_3(g) \longleftarrow 2NH_3(a)+2NH_4^+HCrO_4^-$$
$$\qquad\qquad\qquad\qquad\quad \downarrow$$
$$H_2O(g) \longleftarrow H_2O(a)+(NH_4)_2Cr_2O_7$$
$$\qquad\qquad\qquad\qquad\quad \downarrow$$
$$(NH_4)_2Cr_2O_7,$$

where (a) and (g) indicate adsorbed and gaseous states, respectively.

The reaction begins with the transfer of a proton from NH_4^+ to CrO_4^-. After the proton transfer process is accomplished through a transition state (II), coulombic interaction between NH_3 and $H\text{-}CrO_4^-$ (NH^+) is lost, and NH_3 becomes free to migrate over the surface of the crystal as a mobile adsorbed phase. Then, NH_3(a) will be desorbed, followed by the desorption of H_2O(a). The total pressure showed 7 Torr at 70°C. Therefore the decomposition reaction of the first step takes place at this temperature, where the ratio of NH_3 to H_2O is approximately 2: 1.

Second Decomposition Step. It is seen from Fig. 1 that N_2 and N_2O begin to be evolved at 100°C and the fraction of NH_3 decreases rapidly with increasing temperature. Although the amount of H_2O is large at this temperature, it is less than that produced from oxidation of NH_3 into N_2 and N_2O. It is concluded from the total pressure measurements that the second decomposition step for AC begins at about 150°C. The total pressure increases greatly above this temperature, and amounts to 2.2 Torr at 200°C. At this temperature the evolved gases consist of about 52% N_2O, 21% N_2, 26% H_2O, and NH_3 of less than 1%. Nitrogen content decreases to about 3% at 250°C, while CO_2 begins to be evolved at this temperature. Amounts of CO_2 and N_2O were determined by comparing their pattern coefficients with the corresponding standard ones (Ref. 4 and Table 1). The production of CO_2 is considered to be due to the oxidation of carbon or carbon compounds as impurity in the sample.

The second step in AC decomposition corresponds to the first step for ADC. Many studies have been reported on the ADC decomposition at the temperature range of 180 to 230°C, but these results are not in agreement with each other. Simpson *et al.*[2] have reported that N_2, N_2O, and H_2O were evolved throughout the reaction but free ammonia (10%) was produced at the autocatalytic stage. In the present work, the evolution of NH_3 in the ADC decomposition at 200°C is observed in the beginning but the amount is very

6) J. V. Davies, P. W. M. Jacobs, and A. Russell-Jones, *Trans. Faraday Soc.*, **63**, 1737 (1967).

small as is shown in Table 3. The reason of the discrepancy may be explained by the difference of experimental condition: that is, Simpson used a single crystal as a starting material after evacuation at room temperature and temperature was raised rapidly to 195.5°C, while, in the present work, powdered sample was used and heating rate was rather slower than that adopted by Simpson. The evolution of NH_3 is small, as is shown in Fig. 2. Namely, most of NH_4^+ ions are oxidized from the beginning.

It was concluded from the thermal analysis that CrO_3 are produced by the decomposition of ADC. CrO_3 is a strong oxidizing agent and it is said that hydrogen itself, ammonia and hydrogen sulfide are oxidized by CrO_3.[7] Therefore, NH_3 produced in the crystal will be easily oxidized to form N_2 and N_2O, and consequently Cr(VI) is reduced to lower oxidation state. It is seen that nearly equal amounts of N_2 and N_2O are obtained in evacuating system when the powdered sample is used, as shown in Fig. 3(a), but the amount of N_2 exceeds slightly that of N_2O, when the crystal grain is used, as shown in Fig. 3(b), although the amounts of NH_3 in both cases are quite small as in the case of the closed system. This might be explained by the fact that most of NH_4^+ ions are oxidized as soon as the decomposition proceeds, and the amount of NH_3 which is oxidized after evolution is small. The formation of H_2O continues throughout the decomposition. This is in agreement with Simpson's results. It is expected that Cr(VI) ought to be reduced partly at this step because of the vigorous oxidation of NH_3. However, from the results of X-ray analysis[1] and the measurement of dissociation pressure of CrO_3, it is supported that the product formed in this decomposition step is mainly CrO_3.

Third Decomposition Step. The third step of the decomposition involves the formation of O_2 from the relatively unstable CrO_3. At the temperature near 250°C N_2O and H_2O are the main products and CO_2 is also found. Origin of N_2O and H_2O may be NH_3, NH_2, or N_2 remained in the crystal. The peak of oxygen does not appear at 300°C but appears at 350°C and the amount of CO_2 approaches to 64%. Accordingly the weight decrease at this decomposition step are related to the elimination of O_2, CO_2, H_2O, and N_2O. The evolution of oxygen begins after the production of CO_2 and N_2O are finished, as shown in Figs. 4(a) and 4(b). It seems that oxygen molecules produced by decomposition is consumed for the oxidation of nitrogen compounds and carbon impurities.

Fourth Decomposition Step. The constituents of gases evolved at 400°C are mainly O_2, CO_2, CO, H_2O, and the trace of N_2O. The decomposition takes place between 400 and 450°C as observed in the thermal analysis and the total pressure measurement. The gases evolved at 450°C are mainly O_2, CO, and CO_2 but N_2O is hardly seen. A small amount of NO was observed in this temperature range only when the decomposition was carried out in evacuating system.

Gases Evolved in ADC Decomposition. According to Fig. 2, it is seen that the total pressure at 100°C is very low and the amount of NH_3 is smaller than those of N_2 and N_2O. The first decomposition shows the maximum at about 200°C and the evolved gases are N_2 and N_2O. The formation of O_2 is observed at 400°C.

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7) P. C. L. Thorne and E. R. Roberts, "Inorganic Chemistry," (Ephraims), 6th edition, Oliver & Boyd (1954), p. 503.