Thermal Decomposition of Ammonium Salts of Transition Metal Oxyacids. III.[1] Thermogravimetric Analysis of Ammonium Chromate

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Thermal decomposition of ammonium chromate (AC) and ammonium dichromate (ADC) has been studied by means of TG, DTA, and DTG. It showed four steps in thermal decomposition of AC and three steps in that of ADC. Decomposition product in each step of the thermal decomposition was examined by X-ray diffraction method. From the results of both thermogravimetric analysis and X-ray study, it was concluded that the first decomposition product of AC was ADC, the second was CrO_3 and the final product was Cr_2O_3. The third product gave the X-ray patterns of the mixture of Cr_2O_3 and CrO_3, and the mole ratio of O/Cr in the temperature range for the existence of the product (300—390°C) was 2.1—2.0. The kinetics in the second decomposition step for AC and in the first decomposition step for ADC were studied, giving the values of the energy of activation of 24.2 and 22.4 kcal/mol, respectively.

In a preceding paper of this series,[2] it was reported that molybdenum(VI) oxide formed by thermal decomposition of ammonium paramolybdate oxidized ammonia evolved during the thermal decomposition. It is known that ammonia is oxidized more readily by oxyacids of chromium(VI) than those of molybdenum(VI).

Ammonium chromate decomposes slowly to form ammonium dichromate even at room temperature.[3] It is believed that the thermal decomposition of ammonium dichromate can be described by the following simple reaction:[4]

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$$

As the results of studies on isothermal decomposition of ADC, however, several authors noticed that ammonia and oxides of nitrogen were present in appreciable quantities amongst the decomposition products.[5-10] They examined the compositions of evolved gases and final solid products. Unfortunately, their results as to the composition of the final solid product were not in complete agreement with each other. All of them except Harbard investigated isothermal decomposition reactions, and Harbard carried out the decomposition experiment by heating ADC in a closed tube, the gas evolved being collected in a gas burette. Kinetics and mechanism of isothermal decomposition of ADC were studied by Taylor *et al.*[10,11] without using thermogravimetric analysis.

The present study has been undertaken to make clear the entire processes of thermal decomposition of AC and ADC by means of thermogravimetric analysis, to determine the composition and structure of each decomposition intermediate and the temperature range for the existence of each decomposition product, and to examine kinetics of the decomposition reactions.

Experimental

Thermogravimetric Analysis (TG). TG was carried out by using the quartz spring balance described in the preceding paper of this series.[2] AC and ADC (extra pure reagents of Nakarai Chemical Co.) were powdered to the size of 170—200 mesh prior to each measurement. A sample of 10 mg was heated at a rate of 2°C/min. The ambient pressure of the decomposition was 760 Torr.

Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TG), and Derivative Thermogravimetry (DTG). By using the automatic recording thermobalance of Cho Balance Co., DTA, TG, and DTG were carried out simultaneously. A sample of 20 mg was heated at a rate of 3.7°C/min in the ambient pressure of 760 Torr, and α-Al_2O_3 was taken as a reference material for DTA.

Decomposition Rate Measurements. The experimental apparatus for decomposition rate measurements was similar to that used for TG under vacuum.[2] The kinetics of decomposition of AC and ADC were followed by use of the quartz spring balance. A sample of 20 mg was used for the determination of decomposition rates. The decomposition product in the first step of the thermal decomposition of AC was obtained by heating AC up to 120°C and annealing it for several hours under 760 Torr.

X-Ray Analysis. X-Ray patterns of the intermediates in each step of the decomposition reactions were obtained with an automatic recording diffractometer of Shimadzu Seisakusho, Ltd. using CuK_α radiation. Each decomposition intermediate for X-ray analysis was prepared by annealing the corresponding product at the respective temperatures for several hours.

Results

Thermogravimetric Analysis. The results for thermal decompositions of AC and ADC obtained under 760

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1) Part II: This Bulletin, **45**, 2739 (1972).

2) This Bulletin, **45**, 2745 (1972).

3) P. C. L. Thorne and E. R. Roberts, "Inorganic Chemistry," (Ephraims), 6th edition, Oliver & Boyd (1954), p. 507.

4) R. B. Heslop and P. L. Robinson, "Inorganic Chemistry," 3rd edition, Elsevier Publishing Company (1967), p. 666.

5) W. C. Ball, *J. Chem. Soc.*, **95**, 87 (1909).

6) W. M. Hooton, *Proc. Chem. Soc.*, **24**, 27 (1908).

7) E. Moles and A. Gonzalez, *Anal. Fis. Quim.*, **21**, 204 (1923).

8) E. H. Harbard and A. King, *J. Chem. Soc.*, **1938**, 955.

9) K. Fischbeck and H. Springler, *Z. Anorg. Chem.*, **235**, 183 (1938); *ibid.*, **241**, 209 (1939).

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

11) D. Taylor, *ibid.*, **1955**, 1033.

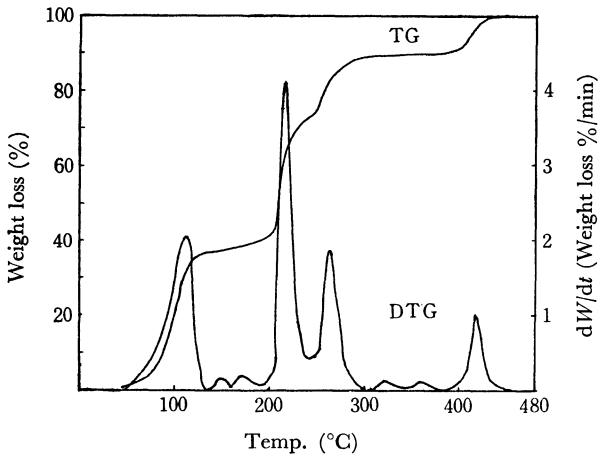

Fig. 1. Thermogravimetric and derivative thermogravimetric curves of AC (in 1 atm.).

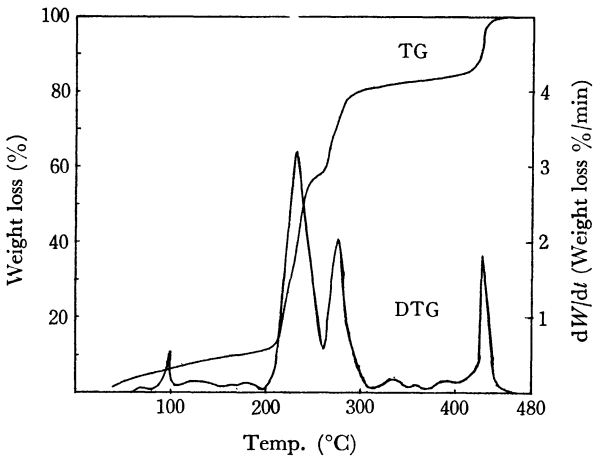

Fig. 2. Thermogravimetric and derivative thermogravimetric curves of ADC (in 1 atm.).

Torr are shown in Figs. 1 and 2, respectively. From these results it is seen that the decomposition of AC proceeds in four steps and that of ADC in three steps. The first step of the decomposition of AC produces an orange-colored ADC, and three succeeding steps of decomposition of AC are similar to the three steps of decomposition of ADC itself.

Differential Thermal Analysis, Thermogravimetric Analysis, and Derivative Thermogravimetry. The results of studies on thermal decomposition of AC and ADC obtained by simultaneous measurement of DTA, DTG, and TG are shown in Figs. 3 and 4. The TG and DTG curves obtained by this method are in good agreement with those obtained by the spring balance method (Figs. 1 and 2). It is seen that the first step of the decomposition of AC is endothermic, whereas the other three steps of the decomposition are exothermic. In this case again the decomposition after the first step of AC is similar to that of ADC itself.

Rate of Decomposition of AC and ADC. About 10—20 min were required for the reaction vessel and reactants to reach a desired constant temperature. The decomposition rates of AC in the second step and those of ADC in the first step were measured at constant temperatures from 180 to 200°C. The rate

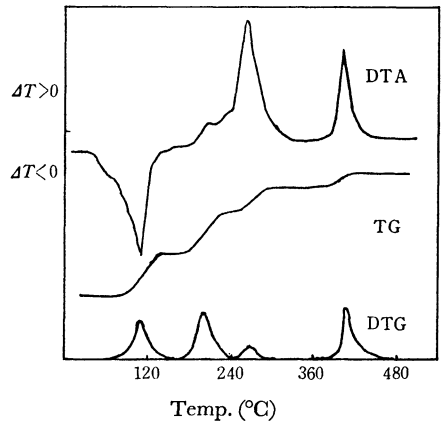

Fig. 3. DTA, TG, and DTG curves of AC.

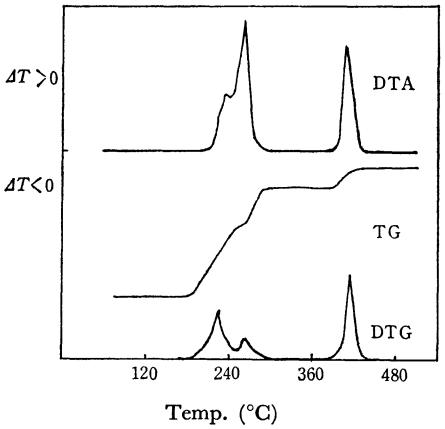

Fig. 4. DTA, TG, and DTG curves of ADC.

determination was followed until the plots of fraction decomposed (α) *vs.* time (t) reached to the end of sigmoid part.

X-Ray Analysis. A sample of AC was heated up to 120°C and annealed for several hours and its X-ray pattern was examined. Another sample of AC was heated up to 240°C and annealed for several hours and its X-ray pattern was examined. The first column-(a) and the third column(c) in Table 1 show the diffraction data of the intermediates prepared by heating AC at 120 and 240°C, respectively. These results are indicated to be almost in agreement with literature values, which are shown in the second (b) and fouth columns(d),[12] respectively. A sample of AC was heated up to 360°C and annealed for several hours, and its X-ray pattern was examined. The results are in the fifth column(e) in Table 1, which represents a pattern entirely different from that of CrO_2,[13] but indicates the presence of both CrO_3 and Cr_2O_3. A sample of AC was heated up to still higher temperature and annealed for several hours to form the final decomposition product, and its X-ray pattern was checked. The final product gave the diffraction data as shown in the sixth column(f), agreeing with those in the literature.[12]

12) S. Kato and K. Kubo, "Chemical Analysis by X-ray Diffraction," Nikkan Kogyo Shinbunsha (1955), pp. 134 and 159.

13) R. S. Schwartz, I. Fankunchen, and R. Ward, *J. Amer. Chem. Soc.*, **74**, 1676 (1952).

TABLE 1. X-RAY DIFFRACTION DATA FOR DECOMPOSITION PRODUCTS OF AC
(a) this study (sample heated in air for several hours at 120°C),
(c) this study (sample heated in air for several hours at 240°C),
(e) this study (sample heated in air for several hours at 360°C),
(f) this study (the final decomposition product of AC),
(b) ADC, (d) CrO_3, and (g) Cr_2O_3 data, Kato and Kubo.[12]

(a)		(b)		(c)		(d)		(e)		(f)		(g)	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
6.61	0.12	6.60	0.58	4.53	0.16			4.23	0.24	3.63	0.25	3.63	0.45
5.13	1.00	5.10	1.00	4.31	0.25			4.17	0.32	2.67	0.67	2.67	0.70
4.61	0.17			4.19	0.41	4.20	0.75	3.72	0.21	2.48	0.90	2.47	0.70
4.11	0.50			3.74	0.14			3.65	0.44	2.17	0.33	2.17	0.30
												2.03	0.04
3.65	0.12	3.77	0.16	3.60	0.12			3.38	0.91	1.81	0.58	1.81	0.45
										1.67	1.00	1.67	1.00
3.44	0.37			3.39	1.00	3.40	1.00	2.67	0.76			1.58	0.06
												1.46	0.30
3.35	0.25	3.37	0.83	2.83	0.10	2.86	0.25	2.47	0.94	1.43	0.33	1.43	0.45
												1.29	0.16
3.30	0.37			2.47	0.08			2.27	0.12			1.23	0.06
												1.21	0.06
3.24	0.90			2.40	0.06	2.36	0.20	2.17	0.44			1.17	0.05
						2.25	0.20					1.15	0.06
3.16	0.29			2.15	0.04			1.81	0.29			1.12	0.06
		3.04	0.40									1.09	0.12
2.97	0.29			2.00	0.06	2.00	0.07	1.71	0.12			1.04	0.10
						1.96	0.10					1.02	0.02
2.77	0.20	2.77	0.27	1.82	0.10	1.84	0.05	1.67	1.00			0.95	0.06
		2.48	0.30			1.74	0.15						
2.32	0.25	2.33	0.18			1.71	0.03	1.58	0.15				
						1.68	0.01						
2.05	0.17	2.05	0.25			1.60	0.03	1.46	0.21				
		2.00	0.10			1.56	0.01						
1.82	0.13	1.92	0.10			1.54	0.01	1.43	0.38				
								1.33	0.09				
1.81	0.13	1.82	0.25										
		1.50	0.10										

Discussion

Thermal Analysis. The composition of each intermediate of the thermal decomposition was determined, and the temperature range where each intermediate existed was deduced from the TG and DTG curves. The decomposition processes are summarized as follows:

Ammonium chromate:

$$(NH_4)_2CrO_4 \xrightarrow{80\text{—}120^\circ C} (NH_4)_2Cr_2O_7\text{(orange)}\ 17.6\%(17.4\%)^{14)} \xrightarrow{200\text{—}230^\circ C} CrO_3\text{(brown)}\ 34.7\%(34.2\%) \xrightarrow{260\text{—}275^\circ C} CrO_2\text{(black)}\ 44.5\%(44.6\%) \xrightarrow{400\text{—}435^\circ C} Cr_2O_3\text{(dark green)}\ 49.1\%(50.0\%)$$

Ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \xrightarrow{205\text{—}245^\circ C} CrO_3\text{(brown)}\ 22.0\%(20.6\%) \xrightarrow{260\text{—}285^\circ C} CrO_2\text{(black)}\ 32.4\%(33.3\%) \xrightarrow{410\text{—}435^\circ C} Cr_2O_3\text{(dark green)}\ 38.5\%(39.7\%)$$

14) The values are weight loss percentages observed, the theoretical values being included in parentheses.

The values of weight loss percentage observed are consistent with the theoretical values within 1%. DTG curve shows a small weight decrease in ADC prior to the first decomposition step, as shown in Fig. 2. This is considered to be due to the removal of adsorbed water from the crystal surface. The percentage of the weight decrease amounts to about 3.5%.

According to the DTA curve of AC, the endothermic peak appears at $T_{max}=110°C$ and the three exothermic peaks appear at $T_{max}=210$, 255, and 410°C, respectively. These temperatures are in good agreement with the temperatures at dw/dt=max. the on DTG curve determined by spring balance measurement.

It was confirmed by thermal analysis that AC decomposes in four steps, and the results of X-ray analysis for the intermediate of each step support the production of the above mentioned compounds. Namely, the first decomposition product from AC at about 120°C is ADC and the second decomposition product formed by heating AC up to 240°C is CrO_3. The product yielded by heating AC up to 360°C corresponds to one having formula of CrO_2 according to the result of weight loss determined by TG, and to the mixture of CrO_3 and Cr_2O_3 according to the X-ray analysis

(Table 1). Thus, the 3.38 Å line might be attributed to CrO_3 and the other strong lines (3.65, 2.67, 2.47, and 1.67 Å) are attributed to Cr_2O_3.

It can be said that an oxide which has the composition of Cr_5O_9 is formed in decomposition of CrO_3 to Cr_2O_3 and this oxide is generally regarded as a double compound of chromium(III) and chromium(VI) oxides, or chromium(III) chromate: $Cr_5O_9=2Cr_2O_3\cdot CrO_3$. The existence of Cr_5O_9 is, however, doubtful. King could not made Cr_5O_9, at least, in the thermal degradation of CrO_3, but he found two non-Daltonide compounds as the intermediates, one of which had 2.6—2.2 and the other 1.9—1.7 atoms of O per atom of Cr.[15] $2Cr_2O_3\cdot CrO_3$ is brown and paramagnetic, CrO_2 is black and both are insoluble in water.[3] On the other hand Taylor[16] has mentioned that CrO_3 melts at 193°C and forms brown chromic chromate ((CrO_2)-$CrO_4=Cr_3O_6$) and liberates oxygen at 250°C,

$$6CrO_3 = 2Cr_3O_6 + 3O_2$$

and on further heating yields chromium sesquioxide.

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$

In the present work, the product obtained when AC was heated up to 360°C showed the composition of CrO_2 and had black color. However, it might be considered that during annealing at 360°C for several hours, some amounts of oxygen was lost by decomposition, a part of which oxidized residual nitrogen compounds or carbon impurity contained in sample, giving lower oxide, Cr_5O_9. Although it has been reported that there are oxides having the various compositions, *e.g.*, Cr_3O_8, Cr_2O_5 *etc.*,[17] none of these have been actually found in this work. The value of the ratio of O/Cr is calculated to be 2.1—2.0 at the temperature range of 300—390°C.

Reaction Kinetics. In order to examine the result of thermal analysis, the decomposition rate of the first step degradation product of AC was compared with that of ADC. Namely, the reaction rates of CrO_3 formation from these samples were measured in isothermal decomposition. The α *vs.* t curves were sigmoid in shape and were analyzed by use of the modified Prout-Tompkins equation:[18]

$$-\ln(1-\alpha) = kt$$

where α is the fraction decomposed in time t and k is the rate constant. The plots of $-\ln(1-\alpha)$ *vs.* t at various temperatures for the decomposition product in the first step of the thermal decomposition of AC and for ADC are shown in Figs. 5 and 6. The results clearly indicate that both reactions follow the unimolecular decay law. Arrhenius plots for the two reactions

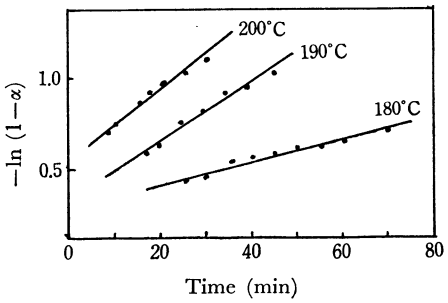

Fig. 5. The plot of $-\ln(1-\alpha)$ *vs.* t for ADC prepared by heating AC up to 120°C.

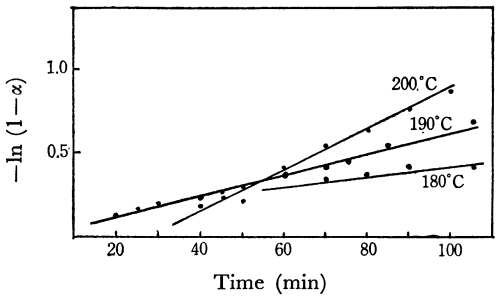

Fig. 6. The plot of $-\ln(1-\alpha)$ *vs.* t for ADC.

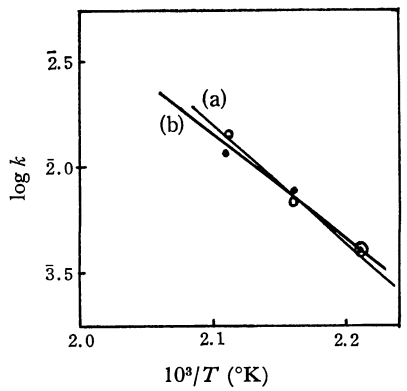

Fig. 7. Arrhenius plots of the rate constants.
(a) in 2nd decomposition step of AC
(b) in 1st decomposition step of ADC

are shown in Fig. 7. From the slopes of these lines, the activation energies of the two reactions are found to be 24.2 and 22.4 kcal/mol, respectively. From these results it may be said that the second step of AC decomposition corresponds to the first step of ADC decomposition, which is in agreement with the conclusion of X-ray analysis.

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15) H. Remy, "Treatises on Inorganic Chemistry," Vol. II, Elsevier (1956), p. 31.
16) F. Sherwood Taylor, "Inorganic and Theoretical Chemistry," 9th edition, Heinemann (1952), p. 672.
17) B. Kubota, *J. Amer. Ceram. Soc.*, **44**, (5), 239 (1961).
18) E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, **40**, 488 (1944); *ibid.*, **42**, 468 (1946).