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The Thermal Decomposition of Vanadium(III) Chloride Oxide and Its Reaction with Oxygen

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The thermogravimetry and differential thermal analysis of VClO in an argon stream were carried out. The products obtained by heating VClO in an argon stream at various temperatures were examined by chemical analysis and X-ray analysis. Also, the reaction between VClO and oxygen was examined in the same manner. When VClO is heated in an argon stream, it decomposes above about 400 °C to form V_2O_3 and VCl_3, $3VClO(s) \rightarrow V_2O_3(s)+VCl_3(s)$. Subsequently, the resulting VCl_3 disproportionates to form VCl_2 and VCl_4, $2VCl_3(s) \rightarrow VCl_2(s)+VCl_4(g)$. VClO reacts with oxygen above about 120 °C to form V_2O_5 and VCl_3O, $6VClO(s)+3O_2(g) \rightarrow 2V_2O_5(s)+2VCl_3O(g)$; this reaction is accompanied by the $4VClO(s)+3O_2(g) \rightarrow 2V_2O_5(s)+2Cl_2(g)$ reaction.

As regards the thermal decomposition of vanadium(III) chloride oxide(VClO), McCarley and Roddy¹⁾ have examined the thermal stability of VClO at a pressure of *ca.* 10^{-3} mmHg in the course of their investigation of the reduction of vanadium(V) trichloride oxide(VCl_3O) with hydrogen, and have estimated that, when VClO is heated, the $3VClO=V_2O_3+VCl_3$ and $6VClO=2V_2O_3+VCl_2+VCl_4$ reactions probably occur simultaneously above 650 °C, although at a higher temperature the latter reaction should become relatively more important since vanadium(III) chloride (VCl_3) becomes increasingly unstable with an increase in the temperature. Schäfer and Wartenpfuhl²⁾ have briefly reported that, when VClO is heated at a pressure of 10^{-5} mmHg, the thermal decomposition of VClO occurs above 620 °C. In addition to these reports, Oppermann³⁾ has reported that the thermal decomposition of VClO, $7VClO(s)=2V_2O_3(s)+2VCl_2(s)+VCl_3O(g)$, occurs above 600 °C; he has also given the equilibrium pressure of the above reaction in the temperature range of 750—850 °C, based on vapor-pressure measurements by a static method using a Bourdon-type sickle gauge. As has been mentioned above, the thermal decomposition of VClO was not clarified. Also, there has been no report on the reaction between VClO and oxygen.

In this paper, the thermal decomposition process of VClO in an argon stream and the reaction process between VClO and oxygen will be revealed.

Experimental

The VClO used was obtained by heating vanadium(IV) chloride oxide (VCl_2O) at 370 °C in an argon stream, based on the results of a previous investigation concerning the disproportionation of VCl_2O;⁴⁾ it was confirmed to be VClO⁵⁾ by X-ray analysis. The chemical analysis gave V, 49.8; Cl, 34.6% (Calcd for VClO: V, 49.75; Cl, 34.62%). VCl_3 was obtained by the thermal decomposition of VCl_4, which had been prepared by the reaction between vanadium (V, 99.8% up) and chlorine at 500 °C,⁶⁾ at 180 °C in an argon atmosphere;⁷⁾ it was confirmed to be $VCl_3$⁸⁾ by X-ray analysis. The chemical analysis gave V, 32.4; Cl, 67.6% (Calcd for VCl_3: V, 32.38; Cl, 67.62%). The oxygen was dried by passing it through concd sulfuric acid and over phosphorous(V) oxide.

The sensitivity of the quartz helix used for the thermogravimetry(TG) was approximately 67 mm/g. 0.15—0.20 g of the sample was heated at a rate of 2.5 °C/min. The flow-rate of argon or oxygen was maintained at 50 cm³/min. The differential thermal analysis (DTA) was performed in an argon stream at the same heating rate for TG. α-Al_2O_3 was used as a reference.

The X-ray analysis of the solid sample was performed using Ni-filtered Cu radiation. The sample chamber of the diffractometer was maintained under a dry nitrogen atmosphere to prevent the contamination of the sample with moisture in the air during the irradiation.

The products obtained by heating VClO in an argon stream at various temperatures were examined by the following procedures. The sample (1.0 g) in a quartz boat (60 mm length, 13 mm width, 7 mm depth) was placed in a straight reaction tube (16 mm i.d.) with a water-cooled condenser. Argon was introduced into the reaction tube at a flow-rate of 50 cm³/min. The sample part was then placed in the centre of an electric furnace (300 mm in heating length) maintained at a specified temperature for a specified period. The temperature of the sample part was controlled to within ±2 °C.

The products obtained by heating VClO in an oxygen stream at various temperatures were examined in the manner described above, except that oxygen was introduced into the reaction tube instead of argon at the same flow-rate as that of argon.

The liquid product (VCl_4 or VCl_3O) was collected in a trap cooled in solid carbon dioxide through the condenser. The chlorine formed was absorbed in a KI solution through the trap and was determined by iodometry. The total amount of chlorine formed during the reaction was determined by adding the above value and the amount of chlorine dissolved in the liquid product in the trap cooled in solid carbon dioxide.⁹,¹⁰⁾ The determination of the amount of chlorine dissolved in the liquid product will be described later.

The chemical analysis of solid and liquid products was performed as follows. The vanadium content in the sample was determined by chelatometric titration,¹¹⁾ while the chlorine content was gravimetrically determined as AgCl after dissolving the sample in dilute nitric acid. When the sample contained vanadium chloride, the chloride oxide, and the oxide, the water-soluble chloride (VCl_2, VCl_3) was dissolved in water and filtered, and the water-insoluble residue (V_2O_3, unreacted VClO) was dissolved in dilute nitric acid. The vanadium and chlorine contents in the both solutions were determined as has been described above.

The amount of chlorine dissolved in the liquid product in the trap cooled in solid carbon dioxide was determined as

Table 1. Thermal decomposition products of VClO in an argon stream

Temp/°C	Heating time/h	Product/% In the boat V_2O_3	VCl_2	VCl_3	Outside the heating zone VCl_4	VCl_3	Cl_2	Unreacted VClO/%
420	6	5	2	<1	3	<1	<0.1	89
700	1	28	11	—	16	2	0.4	42

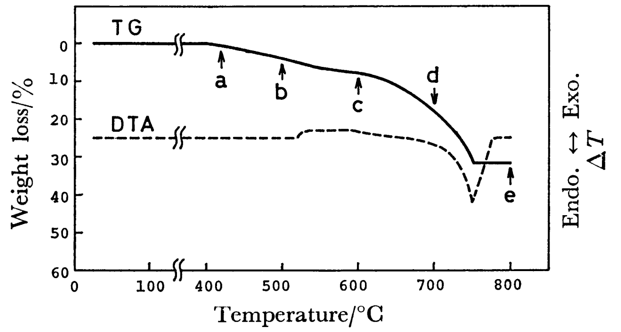

Fig. 1. TG and DTA curves of VClO in an argon stream.

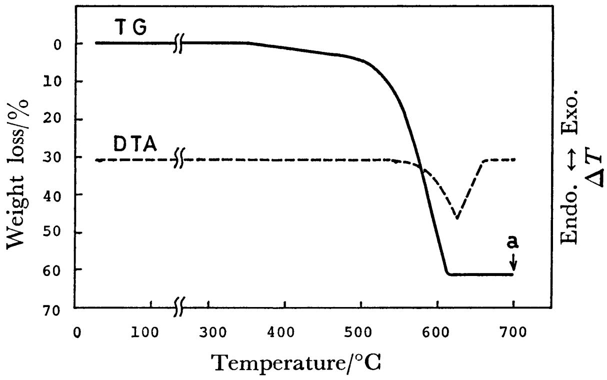

Fig. 2. TG and DTA curves of VCl_3 in an argon stream.

follows. After the reaction was over, the liquid product was allowed to warm to room temperature in an argon atmosphere in order to liberate the chlorine from the liquid product. The liberated chlorine was absorbed in a NaOH solution. A small amount of the liquid product which vaporized during the above procedure was also absorbed in the NaOH solution. The total amount of chlorine in the NaOH solution was gravimetrically determined as AgCl, while the vanadium content in the NaOH solution was also determined by chelatometric titration. From the vanadium content, the amount of the liquid product absorbed in the NaOH solution was calculated. The amount of chlorine dissolved in the liquid product was calculated by subtracting the amount of chlorine corresponding to the liquid product absorbed in the NaOH solution from the total amount of chlorine in the NaOH solution. Also, the total amount of the liquid product formed was corrected by adding the amount of the liquid product absorbed in the NaOH solution to the amount of the liquid product in the trap.

Throughout this work, the chlorides and chloride oxides of vanadium were handled in an argon atmosphere or *in vacuo* to prevent any contamination with moisture.

Results and Discussion

Thermal Decomposition Process of Vanadium(III) Chloride Oxide in an Argon Stream. The TG and DTA curves of VClO in an argon stream are shown in Fig. 1.

The TG curve showed that VClO gradually lost weight above about 400 °C. The samples heated up to Point a (420 °C), Points b (500 °C) and c (600 °C), Point d (700 °C), and Point e (800 °C) in Fig. 1 were found by X-ray analysis to be VClO, a mixture of vanadium(III) oxide(V_2O_3)[12] and unreacted VClO, a mixture of V_2O_3, VCl_2,[13] and unreacted VClO, and a mixture of V_2O_3 and VCl_2, respectively. A weak exothermic effect followed by an endothermic peak was observed in the DTA curve. The weight loss at Point e in Fig. 1 was 31.4%. This value was in good agreement with the calculated value, 31.37%, based on the assumption that the $3VClO(s) \rightarrow V_2O_3(s) + VCl_3(s)$ and $2VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$[14-17] reactions occur when VClO is heated. However, VCl_3 was not observed by X-ray analysis.

Then, the products formed by heating VClO at various temperatures for a specified period were examined by chemical analysis and X-ray analysis. The results are shown in Table 1. The amount of each product is shown as a weight percentage of the product to the initial weight of VClO.

The results showed that a small amount of VCl_3 was formed as a solid product, in addition to V_2O_3 and VCl_2, at 420 °C. The gaseous product formed was confirmed to be VCl_4. Also, the formation of small amounts of VCl_3 and chlorine outside the heating zone was considered to be due to the thermal decomposition of the gaseous VCl_4 formed, $2VCl_4(g) \rightarrow 2VCl_3(s) + Cl_2(g)$,[18] since the molar ratio of the amount of VCl_3 to that of chlorine was calculated to be approximately 2 : 1.

From the above-mentioned results, the solid products on heating VClO were found to be V_2O_3, VCl_2, and VCl_3. Among these products, VCl_3 is unstable on heating. It has been reported that, when VCl_3 is heated, the disproportionation, $2VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$, occurs above 380 °C,[14] 400 °C,[15] 425 °C,[16] or 450 °C.[17]

To confirm the disproportionation of VCl_3, the following experiments were carried out.

The TG and DTA curves of VCl_3 in an argon stream are shown in Fig. 2. The TG curve showed that VCl_3 gradually lost weight above about 350 °C. The sample heated up to Point a (700 °C) in Fig. 2 was found by X-ray analysis to be VCl_2. The weight loss at Point a was 61.3%. This value was in good agreement with the calculated value, 61.27%, based

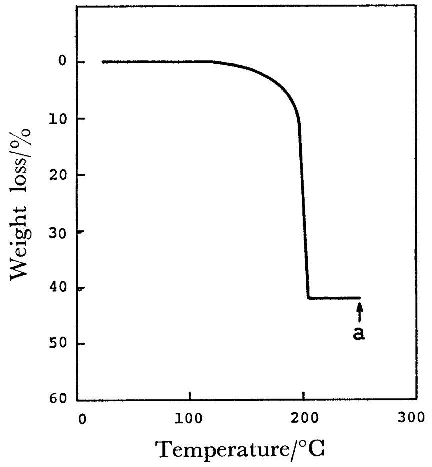

Fig. 3. TG curve of VClO in an oxygen stream.

on the disproportionation of VCl_3, $2VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$. Also, the gaseous product was confirmed to be VCl_4 by the chemical analysis of the product obtained outside the heating zone by heating VCl_3 (1.0 g) in an argon stream at 600 °C for 1 h.

From these results, it is clarified that VCl_3 disproportionates above about 350 °C with an endothermic effect, according to the $2VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$ reaction.

Considering the above-mentioned results, it is found that, when VClO is heated in an argon stream, the $3VClO(s) \rightarrow V_2O_3(s) + VCl_3(s)$ reaction occurs above about 400 °C. Subsequently, the resulting VCl_3 disproportionates according to the $2VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$ reaction, since the disproportionation of VCl_3 occurs as early as about 350 °C.

The exothermic effect observed in the DTA curve, shown in Fig. 1, is considered to be due to the $3VClO(s) \rightarrow V_2O_3(s) + VCl_3(s)$ reaction, since the disproportionation of VCl_3 is accompanied by an endothermic effect. It was considered that the observed exothermic effect was very weak, because the $3VClO(s) \rightarrow V_2O_3(s) + VCl_3(s)$ reaction proceeded slowly at the lower temperature and was accompanied by the disproportionation of the resulting VCl_3, with an endothermic effect.

As has been mentioned above, Oppermann[3] has reported that the thermal decomposition, $7VClO(s) \rightarrow 2V_2O_3(s) + 2VCl_2(s) + VCl_3O(g)$, occurs when VClO is heated in a sealed tube. On the other hand, the formation of VCl_3O was not observed on heating VClO in an argon stream. It may be considered that the VCl_3O was formed by the reaction between unreacted VClO and gaseous VCl_4,[2] which had itself been formed *via* the thermal decomposition of VClO, as has been revealed in this work.

Reaction Process between Vanadium(III) Chloride Oxide and Oxygen. The TG curve of VClO in an oxygen stream is shown in Fig. 3.

The results showed that VClO reacted with oxygen before decomposing and that the reaction proceeded rapidly above about 200 °C. The sample heated up to Point a (250 °C) was found by X-ray analysis to be a mixture of vanadium(V) oxide(V_2O_5)[19] and a small amount of vanadium(IV) oxide(VO_2).[20]

TABLE 2. REACTION PRODUCTS BETWEEN VClO AND OXYGEN AT VARIOUS TEMPERATURES

Temp/°C	Reaction time/h	Product/% In the boat V_2O_5	Product/% In the boat VO_2	Product/% Outside the heating zone VCl_3O	Product/% Outside the heating zone Cl_2	Unreacted VClO/%
120	0.5	<1	—	0.2	<0.1	>99
	1	<1	—	0.4	0.1	99
	3	2	—	1.2	0.3	97
150	0.5	2	—	1.2	0.2	97
	1	5	—	3.6	0.5	92
	3	9	—	5.6	1.2	86
170	0.5	5	—	4.1	0.3	91
	1	8	—	6.6	0.4	87
	3	22	—	16.5	1.7	64
190	0.5	26	<1	21.3	1.3	57
	1	40	2	34.5	2.4	31
	3	55	4	48.1	3.4	3
200	0.5	42	15	51.9	1.6	2
230	0.5	46	13	52.3	1.9	0
250	0.5	52	7	52.5	1.9	0

TABLE 3. SOLID PRODUCTS BETWEEN VClO AND OXYGEN AT VARIOUS FLOW-RATES OF OXYGEN

O_2 flow-rate / $cm^3\ min^{-1}$	Solid product/% V_2O_5	Solid product/% VO_2	Unreated VClO/%
50	89	9	2
100	94	5	1
200	>99	—	<1

To obtain more detailed information on the reaction between VClO and oxygen, the products formed by heating VClO for a specified period at various temperatures in an oxygen stream were examined by X-ray analysis and chemical analysis.

At 110 °C, no reaction product was observed. The reaction products obtained at various temperatures above 120 °C and their weight percentages relative to the initial VClO were determined by chemical analysis and X-ray analysis.[5,19,20] The results are shown in Table 2.

These results indicate that the reaction between VClO and oxygen proceeds above about 120 °C. V_2O_5, VCl_3O, and a small amount of chlorine were formed below 170 °C. Above 190 °C, VO_2 was also formed in addition to these products.

The most stable oxide phase of vanadium under the conditions of this work is V_2O_5,[21] and, as is shown in Table 2, VO_2 was not formed below 170 °C. However, the formation of VO_2 in addition to V_2O_5 was observed above 190 °C. As is shown in Table 2, the reaction between VClO and oxygen proceeded markedly above 190 °C to form a large amount of gaseous VCl_3O. Consequently, the concentration of oxygen decreased temporarily in the neighborhood of the sample VClO in the boat. Under such a low concentration of oxygen, the oxidation of VClO has been thought to yield VO_2. Then, the solid products obtained by heating VClO (0.25 g) at 200 °C under various flow-rates of oxygen for 0.5 h were examined.

The results are shown in Table 3.

From the results, it was observed that VO_2 was not formed under a high flow-rate of oxygen. This confirms the above consideration of the formation of VO_2.

Based on the experimental results presented above, the reaction process between VClO and oxygen will now be discussed.

The experimental results for the reaction products between VClO and oxygen at various temperatures, shown in Table 2, showed that V_2O_5 and VCl_3O were the main products. This fact was considered to indicate that the main reaction which occurred upon heating VClO in an oxygen stream was

$$6VClO(s) + 3O_2(g) \rightarrow 2V_2O_5(s) + 2VCl_3O(g). \qquad (1)$$

The reactions which possibly gave the chlorine (in Table 2) were considered to be

$$4VClO(s) + 3O_2(g) \rightarrow 2V_2O_5(s) + 2Cl_2(g) \qquad (2)$$

and the reaction between gaseous VCl_3O formed by Reaction 1 and oxygen,

$$4VCl_3O(g) + 3O_2(g) \rightarrow 2V_2O_5(s) + 6Cl_2(g).^{22)} \qquad (3)$$

It has previously been reported that Reaction 3 does not proceed below 400 °C.[22] The present authors also confirmed that Reaction 3 began at about 400 °C and proceeded almost completely above about 700 °C. On the basis of these results, the formation of a small amount of chlorine obtained by heating VClO in an oxygen stream was considered to be due to Reaction 2.

Based on the assumption that the formation of chlorine was due to Reaction 2, the amount of V_2O_5 formed by Reaction 2 was calculated from the amount of chlorine formed (in Table 2). The molar ratio of the amount of VCl_3O to the amount of V_2O_5 obtained by subtracting the amount of V_2O_5 formed by Reaction 2 from the total amount of V_2O_5 formed was calculated to be approximately 1 : 1. In this calculation, the amount of VO_2 formed was converted into that of V_2O_5 on the assumption that VO_2 was oxidized to V_2O_5. These results confirmed that the main reaction which occurred when VClO was heated in an oxygen stream was Reaction 1 and that this reaction was accompanied by Reaction 2.

The above-mentioned results reveal that VClO reacts with oxygen above about 120 °C according to Reaction 1 and that this reaction is accompanied by Reaction 2. As a result, V_2O_5 (under a low concentration of oxygen, VO_2 is formed in addition to V_2O_5), VCl_3O, and a small amount of chlorine are formed.

References

1) R. E. McCarley and J. W. Roddy, *J. Inorg. Nucl. Chem.*, **15**, 293 (1960).

2) H. Schäfer and F. Wartenpfuhl, *J. Less-Common Met.*, **3**, 29 (1961).

3) H. Oppermann, *Z. Anorg. Allg. Chem.*, **351**, 127 (1967).

4) A. Yajima, R. Matsuzaki, and Y. Saeki, Preprint of the 37th National Meeting of Chemical Society of Japan, I (1978), p. 36, *Bull. Chem. Soc. Jpn.*, in press.

5) Joint Committee on Powder Diffraction Standards, Powder Diffraction File, 23-1472.

6) C. Starr, F. Bitter, and A. R. Kaufmann, *Phys. Rev.*, **58**, 977 (1940).

7) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 60 (1964).

8) Joint Committee on Powder Diffraction Standards, Powder Diffraction File, 15-382.

9) A. Morette, *C. R. Acad. Sci.*, **202**, 1846 (1936).

10) F. E. Brown and J. E. Snyder, *J. Am. Chem. Soc.*, **47**, 2671 (1925).

11) J. Krtil, *Z. Anal. Chem.*, **219**, 412 (1965).

12) ASTM X-Ray Powder Data File, 1-1293.

13) Joint Committee on Powder Diffraction Standards, Powder Diffraction File, 15-215.

14) P. Ehrlich and H. J. Seifert, *Z. Anorg. Allg. Chem.*, **301**, 282 (1959).

15) H. Funk and W. Weiss, *Z. Anorg. Allg. Chem.*, **295**, 327 (1958).

16) M. A. Oranskaya, Yu. S. Lebedev, and I. L. Perfilova, *Russ. J. Inorg. Chem.*, **6**, 132 (1961).

17) A. B. McIntosh, *Ind. Chem.*, **32**, 195 (1956).

18) J. H. Simons and M. G. Powell, *J. Am. Chem. Soc.*, **67**, 75 (1945).

19) ASTM X-Ray Powder Data File, 9-387.

20) Joint Committee on Powder Diffraction Standards, Powder Diffraction File, 19-1398.

21) H. Endo, M. Wakihara, and M. Taniguchi, *Chem. Lett.*, **1974**, 905.

22) N. I. Vorob'ev, V. V. Pechkovskii, F. N. Kozlov, and Yu. A. Raikov, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, **12** (3), 86 (1969).