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BEHAVIOR OF $MoO_2Cl_2 \cdot H_2O$ ON HEATING

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In an argon stream, $MoO_2Cl_2 \cdot H_2O$ decomposes above 80°C to $HMo_9O_{27}Cl$ and HCl. The $HMo_9O_{27}Cl$ formed decomposes above 205°C to a molybdenum oxide showing a hitherto unknown X-ray diffraction pattern and HCl. The decomposition is accompanied by the sublimation of $MoO_2Cl_2 \cdot H_2O$. In an HCl stream, $MoO_2Cl_2 \cdot H_2O$ sublimes at 50-100°C. The sublimation is accompanied by the decomposition above 150°C.

It has been reported in the early literatures that a molybdenum compound which might be represented as $MoO_2Cl_2 \cdot H_2O$, $MoO(OH)_2Cl_2$, or $MoO_3 \cdot 2HCl$ is obtained by passing gaseous HCl over MoO_3 heated at 200-400°C[1]. Later, it has been reported that this compound is $MoO_2Cl_2 \cdot H_2O$ from the infrared and Raman spectroscopic studies[2,3], and that it crystallizes in an orthorhombic lattice[4,5].

As regards the behavior of $MoO_2Cl_2 \cdot H_2O$ on heating, Graham and Hepler[6] have described that it can be sublimed at 150°C in an HCl stream. Hultgren and Brewer[7] have reported on the basis of vapor pressure measurements that the decomposition of $MoO_2Cl_2 \cdot H_2O$ to MoO_3 and gaseous HCl commences upon heating above 115°C at 475 mmHg vapor pressure of HCl.

In this letter, the behaviors of $MoO_2Cl_2 \cdot H_2O$ on heating in argon and HCl streams will be reported in detail.

A sample of $MoO_2Cl_2 \cdot H_2O$ was prepared by heating MoO_3 at 300°C in a stream of dry HCl, and was confirmed as $MoO_2Cl_2 \cdot H_2O$[4] by X-ray analysis. Chemical analysis of the $MoO_2Cl_2 \cdot H_2O$ gave Mo 44.3%, Cl 32.7%(calcd.: Mo, 44.24%; Cl, 32.7%).

X-ray diffraction data were obtained with an X-ray powder diffractometer, equipped with a proportional counter, using Ni filtered Cu radiation. Molybdenum content in the sample was determined gravimetrically as $PbMoO_4$. Chlorine content in the sample was determined gravimetrically as AgCl or colorimetrically using $Hg(SCN)_2$ and $(NH_4)Fe(SO_4)_2$ solutions.

Behavior of $MoO_2Cl_2 \cdot H_2O$ on Heating in an Argon Stream

The behavior of $MoO_2Cl_2 \cdot H_2O$ on heating was examined by thermogravimetry(TG) and differential thermal analysis(DTA) in an argon stream, the flow-rate of which is 50 ml/min. 0.5 g of $MoO_2Cl_2 \cdot H_2O$ was heated at a rate of 2.5°C/min. The results are shown in Fig. 1.

X-ray powder diffraction data of the sample heated up to 180°C(Point A) are shown in Table 1(A). Chemical analysis of the sample gave Mo 64.7%, Cl 2.6%. When

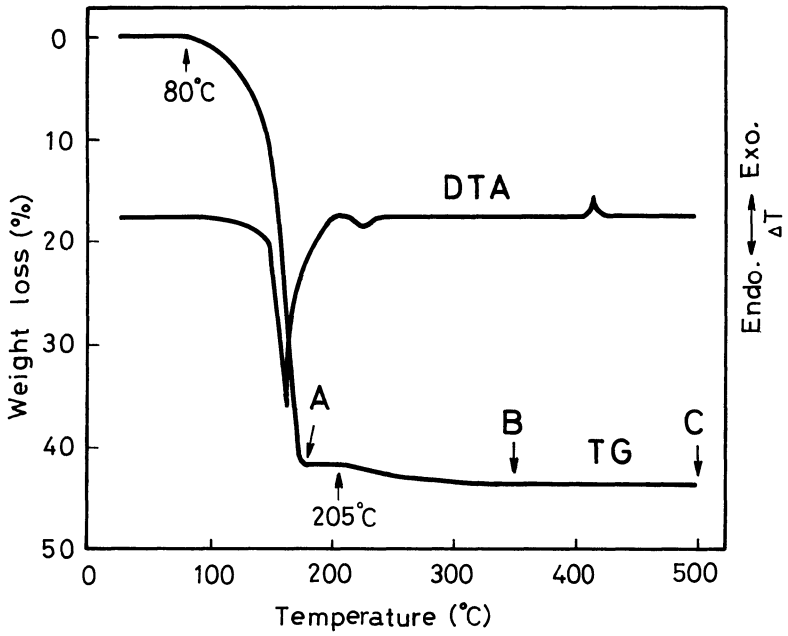

Fig. 1 TG and DTA curves of $MoO_2Cl_2 \cdot H_2O$ on heating in an argon stream

Table 1 X-RAY POWDER DIFFRACTION DATA OF THE SAMPLES OBTAINED BY HEATING $MoO_2Cl_2 \cdot H_2O$ UP TO 180 AND 350°C

(CuKα: λ=1.5418Å)

(A): 180°C		(B): 350°C			
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
3.85	100	3.87	100	1.933	5
3.74	75	3.56	40	1.873	5
3.60	20	3.43	15	1.852	5
3.43	15	3.38	10	1.781	5
3.09	15	2.68	10	1.710	5
2.67	30	2.64	15		
1.859	10	2.59	10		
1.804	10	2.146	5		
1.681	15	2.040	5		

the sample was heated at 350°C in an argon stream, the evolution of gaseous HCl was observed. From these results, the sample seems to be a hitherto unknown compound represented as $9MoO_3 \cdot HCl$, $Mo_9O_{26}(OH)Cl$, $HMo_9O_{27}Cl$, or $Mo_{18}O_{53}Cl_2 \cdot H_2O$ (calcd.: Mo, 64.82%; Cl, 2.66 %). Furthermore, it was found that absorption bands of HCl, H_2O, and OH were lacking in the IR spectrum of the sample. These results indicate that the product obtained by heating $MoO_2Cl_2 \cdot H_2O$ up to 180°C might be represented as $HMo_9O_{27}Cl$.

Chemical analyses of the samples heated up to 350°C(Point B) and 500°C(Point C) gave Mo 66.6%, Cl 0.06%, and Mo 66.6%, Cl 0.02%, respectively(calcd. for MoO_3: Mo, 66.65%). X-ray powder diffraction data of the sample heated up to 350°C are shown in Table 1(B). X-ray analysis of the sample heated up to 500°C showed it to be common MoO_3(orthorhombic[8]). On the other hand, the molybdenum oxide showing X-ray diffraction pattern given in Table 1 (B) was also formed by heating $MoO_2Cl_2 \cdot H_2O$ at 350°C in an oxygen stream, and this pattern is clearly different from that of known MoO_3[8,9].

Furthermore, from the results of DTA and TG combined with X-ray analysis on the molybdenum oxide showing X-ray diffraction pattern given in Table 1(B), it was clarified that a small exothermic peak at 420°C in DTA curve was due to the phase transition of the molybdenum oxide formed by heating $MoO_2Cl_2 \cdot H_2O$ up to 350°C to the common MoO_3(orthorhombic), and that the transition was irreversible.

The weight loss observed when $MoO_2Cl_2 \cdot H_2O$ was heated up to 180°C was higher than the calculated value,31.76%, based on the complete decomposition of $MoO_2Cl_2 \cdot H_2O$ into $HMo_9O_{27}Cl$ and gaseous HCl. This seems to be due to the sublimation of a small

amount of $MoO_2Cl_2 \cdot H_2O$ on heating. The weight loss observed from 205°C to 350°C agreed with the calculated value, 1.55%, based on the complete decomposition of $HMo_9O_{27}Cl$ to MoO_3 and gaseous HCl.

To confirm the above-mentioned estimation on the sublimation of $MoO_2Cl_2 \cdot H_2O$, the following experiments were carried out. 1 g of $MoO_2Cl_2 \cdot H_2O$ in a boat was placed in a reaction tube. The reaction tube was placed in an electric furnace maintained at a specified temperature above 100°C. The sample was heated at an argon flow-rate of 50 ml/min until no more HCl was evolved. Products obtained in the boat and outside the heating zone were examined by X-ray and chemical analyses. Also, the amount of HCl formed by the decomposition of $MoO_2Cl_2 \cdot H_2O$ was examined. The results are shown in Table 2.

Table 2 RESULTS OF HEATING EXPERIMENTS ON $MoO_2Cl_2 \cdot H_2O$ IN AN ARGON STREAM

Temperature	Heating time	In the boat		Outside the heating zone		Amount of HCl formed
(°C)	(hr)	Product	(wt. %)	Product	(wt. %)	(wt. %)
100	13	$HMo_9O_{27}Cl$	61.5	$MoO_2Cl_2 \cdot H_2O$	9.5	28.5
150	5	$HMo_9O_{27}Cl$	60.8	$MoO_2Cl_2 \cdot H_2O$	10.5	28.0
300	2	new form of molybdenum oxide	58.7	$MoO_2Cl_2 \cdot H_2O$	11.5	29.4
350	2	new form of molybdenum oxide	56.4	$MoO_2Cl_2 \cdot H_2O$	14.5	28.7
500	2	MoO_3(orthorhombic)	54.1	$MoO_2Cl_2 \cdot H_2O$	18.0	27.5

From the results, it was confirmed that the decomposition of $MoO_2Cl_2 \cdot H_2O$ was accompanied by the sublimation of $MoO_2Cl_2 \cdot H_2O$.

The results described above show that $MoO_2Cl_2 \cdot H_2O$ begins to decompose at 80°C to $HMo_9O_{27}Cl$ and gaseous HCl. The $HMo_9O_{27}Cl$ formed begins to decompose at 205°C to gaseous HCl and a new form of molybdenum oxide showing X-ray diffraction pattern given in Table 1(B). The decomposition of $MoO_2Cl_2 \cdot H_2O$ is accompanied by the sublimation. Furthermore, the new form of molybdenum oxide transforms irreversibly to the common MoO_3(orthorhombic) at 420°C.

Behavior of $MoO_2Cl_2 \cdot H_2O$ on Heating in a Hydrogen Chloride Stream

The weight change of $MoO_2Cl_2 \cdot H_2O$ on heating was examined in an HCl stream, the flow-rate of which is 50 ml/min, in the same way as described in previous paragraph. The TG curve showed that $MoO_2Cl_2 \cdot H_2O$ lost weight continuously above 50°C and the weight loss reached 100%.

To obtain more detailed information on the behavior of $MoO_2Cl_2 \cdot H_2O$ on heating in an HCl stream, the products obtained by heating 1 g of $MoO_2Cl_2 \cdot H_2O$ at various temperatures for specified periods at an HCl flow-rate of 50 ml/min were examined in the same way as described in previous paragraph. The results are shown in Table 3.

Table 3 RESULTS OF HEATING EXPERIMENTS ON $MoO_2Cl_2 \cdot H_2O$ IN AN HCl STREAM

Temperature (°C)	Heating time (min)	In the boat Product	Yield(g)	Outside the Heating zone Product
100	60	$MoO_2Cl_2 \cdot H_2O$	0.8	$MoO_2Cl_2 \cdot H_2O$
	240	$MoO_2Cl_2 \cdot H_2O$	0.1	$MoO_2Cl_2 \cdot H_2O$
	360	-	-	$MoO_2Cl_2 \cdot H_2O$
150	30	$HMo_9O_{27}Cl$	0.2	$MoO_2Cl_2 \cdot H_2O$
	60	$HMo_9O_{27}Cl$	0.1	$MoO_2Cl_2 \cdot H_2O$
	120	-	-	$MoO_2Cl_2 \cdot H_2O$
200	15	$HMo_9O_{27}Cl$	0.2	$MoO_2Cl_2 \cdot H_2O$
	60	-	-	$MoO_2Cl_2 \cdot H_2O$
300	5	new form of molybdenum oxide	0.2	$MoO_2Cl_2 \cdot H_2O$
	30	-	-	$MoO_2Cl_2 \cdot H_2O$

$MoO_2Cl_2 \cdot H_2O$ sublimed without decomposition at 100°C. The sublimation was accompanied by the decomposition of $MoO_2Cl_2 \cdot H_2O$ above 150°C, giving $HMo_9O_{27}Cl$ at 150-200°C and the new form of molybdenum oxide described in previous paragraph at 300°C. It was also observed that the amount of the decomposition product which remained in the boat decreased with the increase of heating time. But, the product obtained outside the heating zone was $MoO_2Cl_2 \cdot H_2O$ alone. These facts indicate that the decomposition products in the boat reacted with gaseous HCl to form gaseous $MoO_2Cl_2 \cdot H_2O$.

Graham and Hepler[6] have described that $MoO_2Cl_2 \cdot H_2O$ can be sublimed at 150°C in an HCl stream. But, the results of this work show that the process comprises i) the sublimation of $MoO_2Cl_2 \cdot H_2O$, ii) the decomposition of $MoO_2Cl_2 \cdot H_2O$ to $HMo_9O_{27}Cl$ and gaseous HCl, and iii) the formation of gaseous $MoO_2Cl_2 \cdot H_2O$ by the reaction between the $HMo_9O_{27}Cl$ and gaseous HCl.

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