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THE THERMAL DECOMPOSITION OF AMMONIUM HEPTAMOLYBDATE

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ABSTRACT

The thermal decomposition of ammonium heptamolybdate has been investigated by TG. The decomposition is discussed, making use of additional information obtained from isothermal studies, X-ray and IR measurements. The formation of two new compounds, namely $(NH_4)_2O \cdot 14\ MoO_3$ and $(NH_4)_2O \cdot 22\ MoO_3$, prior to the formation of MoO_3 is detected, as well as the main intermediate compounds $(NH_4)_2O \cdot 2.5\ MoO_3$ or $(NH_4)_2O \cdot 3\ MoO_3$ (according to the water content of the starting material) and $(NH_4)_2O \cdot 4\ MoO_3$.

INTRODUCTION

The thermal decomposition of ammonium heptamolybdate has been investigated by a number of authors [1—14]. According to almost all the studies, $(NH_4)_2O \cdot 2.5\ MoO_3$ and $(NH_4)_2O \cdot 4\ MoO_3$ were the most frequently occurring intermediary compounds. Hegedus and co-workers [10] distinguished two new compounds, $(NH_4)_2O \cdot 14\ MoO_3$ and $(NH_4)_2O \cdot 22\ MoO_3$, prior to the formation of MoO_3. Also, $(NH_4)_2O \cdot 3\ MoO_3$ and $(NH_4)_2O \cdot 12\ MoO_3$ have been reported by Schwing-Weill [7]. This clearly indicates a need for further work on this subject.

In the present work, we have re-investigated the thermal decomposition of two different samples, aiming at the elucidation of such compounds. TG, X-ray and IR were used to characterize the different intermediate products. An isothermal study was also applied to establish the role of the water of hydration, included in the starting material, on the thermal decomposition.

EXPERIMENTAL

Chemicals

The ammonium heptamolybdate tetrahydrate samples used in this study were provided by BDH chemicals Ltd. Poole, England (Sample I) and Veb Laborchemie, Apolda, Germany (Sample II).

Apparatus and technique

X-Ray diffraction patterns of the above samples and intermediate products were obtained with the aid of a Phillips unit type PW 1010. The IR study was done in the range 400—4000 cm^{-1}, using the KBr technique and a Carl Jena spectrophotometer. Thermogravimetric analysis was conducted with an automatically recording apparatus, Gebruder Netzsch Selb, W. Germany. Changes in weight were recorded simultaneously with temperature at a rate of 1.25°C min^{-1}. The isothermal study at a series of fixed temperatures was also followed with the thermobalance.

RESULTS AND DISCUSSION

X-Ray data of the two samples used in this work are presented in Table 1. It is seen that X-ray data of sample I are identical with those previously mentioned and correspond to the formula 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot 4\ H_2O$. On the other hand, the *d*-lines obtained for sample II display some differences from

TABLE 1

X-Ray data for ammonium paramolybdate

3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot 4\ H_2O$				3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot H_2O$	
Present work		Schwing—Weill [7]		Present work	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
9.167	100	9.167	s	7.461	7
7.248	32	7.201	s	7.075	35
7.019	64			6.316	77
6.366	24	6.356	m	5.336	14
5.749	10	5.801	w	5.063	40
5.211	8	5.228	w	4.818	40
5.063	6	5.075	w	4.073	10
4.667	6	4.691	w	3.616	50
4.453	12	4.458	m	3.336	100
3.798	12	3.801	m	3.229	65
3.6596	13	3.686	m	3.183	60
3.553	8	3.607	m	3.119	35
3.458	8	3.484	m	3.015	25
3.361	12	3.378	m	2.976	20
3.324	10	3.341	m	2.650	16
3.227	18	3.257	w	2.476	16
3.136	6	3.146	w	2.447	16
3.076	10	3.076	m	2.390	15
2.986	18	2.943	w	2.348	10
2.879	28	2.879	w	2.302	6
2.855	10	2.866	w	2.247	20
2.808	10	2.809	m	2.175	20
2.704	10	2.722	w	2.084	15
2.612	10	2.63	m	1.901	18
2.576	8	2.581	m	1.810	2
2.342	7	2.348	w		
2.231	8	2.237	m		

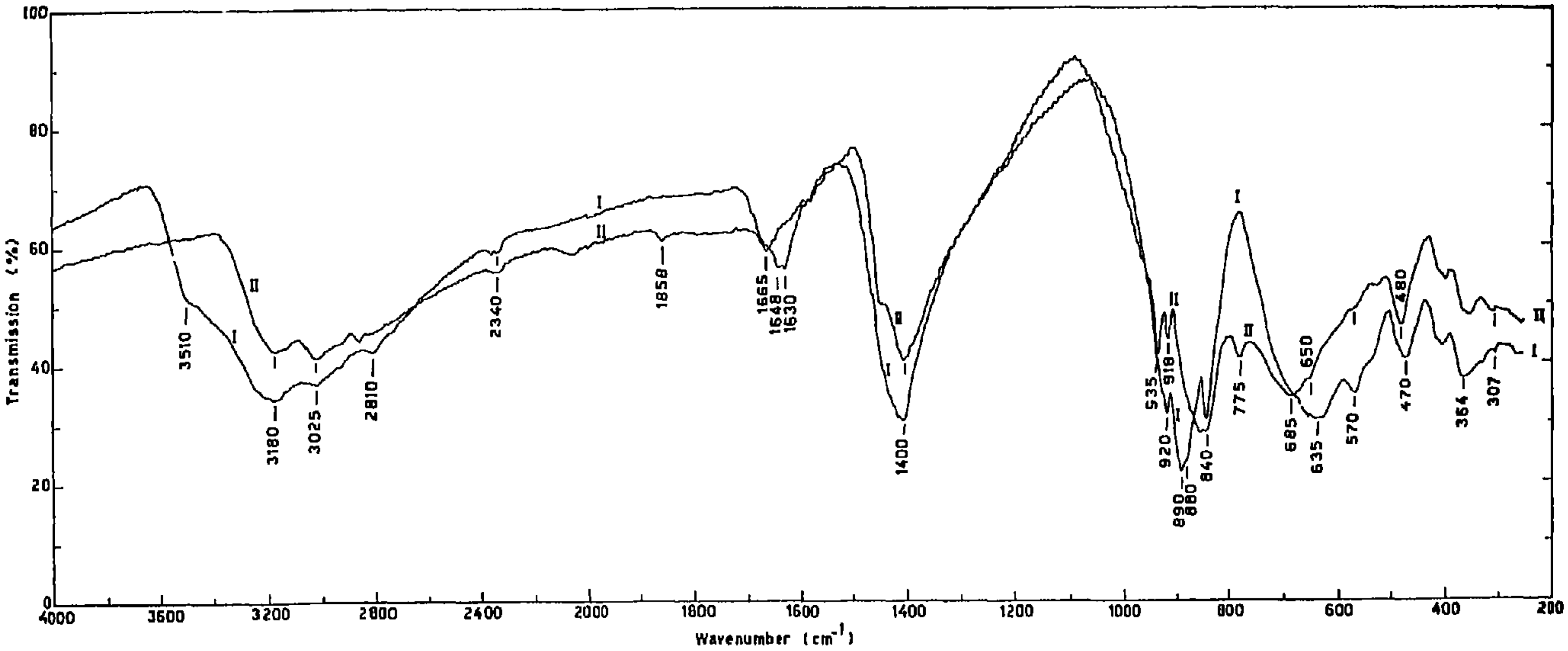

Fig. 1. Infrared spectra of ammonium heptamolybdate. I, 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot 4\ H_2O$; II, 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot H_2O$.

those mentioned above, even from those reported by Louisy and Dunoyer [12] for the di- and anhydrous paramolybdate.

The IR absorption peaks of both samples are shown in Fig. 1 and are reported in Table 3. The absorption bands of sample I agree closely with those of the tetrahydrate given by Schwing-Weill [13]. Those of sample II show two extra absorption bands at 775 and 945 cm^{-1}. The bands at 570 cm^{-1} appears as a shoulder only. The peaks corresponding to the stretching vibrations of MoO_3 are slightly shifted. Thus the bands at 470 and 635 cm^{-1} are shifted to 480 and 685 cm^{-1} respectively. The variation in the absorption peaks is quite clear in the range 840—950 cm^{-1} where the band at 840 cm^{-1} in sample I is split to give two, at 840 and 855 cm^{-1}, and the two bands at 880 and 890 cm^{-1} totally disappear in sample II. The variations exhibited between both samples indicate that the symmetry of the molybdate anion is different. The more pronounced variation is in the range 1600—1700 cm^{-1}, representing the bending vibration of H_2O. In sample I three bands indicate different species of OH groups. A shoulder at 1680 cm^{-1} and its harmonic tone at 3510 cm^{-1} indicate the presence of free water of hydration, which is not the case with sample II. One absorption peak of smaller intensity is observed at 1665 cm^{-1} without any indication of even a shoulder at 3510 cm^{-1}. This is also confirmed from the loss of weight which started at 80°C in the case of sample I. Thus, the four water molecules of sample I include free water, as well as the water of crystallization. The X-ray and IR examinations reflect differences between the two starting materials.

The TG curves in Fig. 2 indicate a total weight loss of 182 mg g^{-1} for sample I, which is in agreement with the theoretical weight loss for $3\,(NH_4)_2O \cdot 7\,MoO_3 \cdot 4\,H_2O$, to give rise to the final product MoO_3. Sample II indicates a total weight loss of 146 mg g^{-1} to achieve the final product MoO_3. This weight loss is less than the theoretical value. By back calculation to the starting material taking the final product MoO_3 (confirmed by X-ray and IR) as a base, the compound might contain one molecule of H_2O, i.e. ($3\,(NH_4)_2O \cdot 7\,MoO_3 \cdot H_2O$ and not $3\,(NH_4)_2O \cdot 7\,MoO_3 \cdot 4\,H_2O$). To be more precise, this sample was supplied many years ago, so storage in Egypt at room temperature which may reach up to 45°C in the summer may lead to a change of the tetrahydrate. Dupuis [6] reported that the tetrahydrate decomposed to $2\,(NH_4)_2O \cdot 5\,MoO_3$ at 48°C. However, examination of the X-ray data of sample II did not indicate the presence of any of the diffraction lines given by Hegedus and co-workers [10] and Schwing-Weill [7] for the compound $2\,(NH_4)_2O \cdot 5\,MoO_3$.

The transformation of the ammonium paramolybdate tetrahydrate to the monohydrate which is proposed to take place in sample II is accompanied with a structural collapse. Some of the water molecules therefore seem to have a coordination function [15]. This is in accord with Evans [16], as the hydrates of poly acids are classified as containing structural water only. Thus sample II may be considered as $3\,(NH_4)_2O \cdot 7\,MoO_3 \cdot H_2O$, having the X-ray and the IR data given in Table 1 and 3.

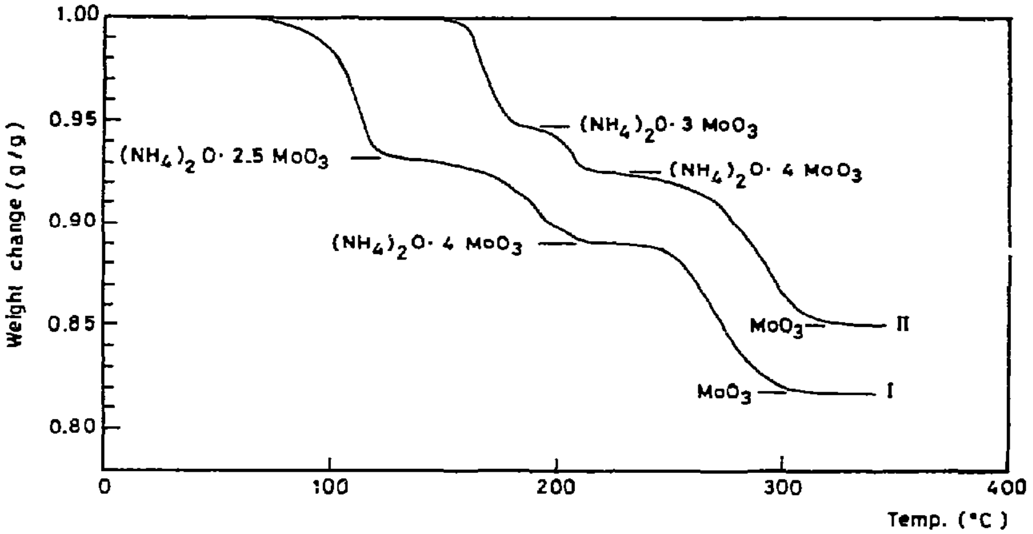

Fig. 2. TG curves for ammonium heptamolybdate. Heating rate, 1.25°C min^{-1}. I, 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot 4\ H_2O$; II, 3 $(NH_4)_2O \cdot 7\ MoO \cdot H_2O$.

Thermogravimetric analysis

Figure 2 shows the TG curves obtained for 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot 4\ H_2O$ and 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot H_2O$. Three well-defined steps are shown from the thermograms and, according to many authors and based on X-ray examination of the end product, the last step corresponds to MoO_3.

Comparison of the two curves reveals some differences in behaviour on heating up to 350°C. Thus for sample I the weight loss in the early stage proceeds rapidly, ending at a plateau which lies in the temperature range 80—110°C, representing the composition $(NH_4)_2O \cdot 2.5\ MoO_3$. This is followed by a further drop ending in a horizontal second plateau in the range 210—230°C, corresponding exactly to $(NH_4)_2O \cdot 4\ MoO_3$.

In sample II there is no weight change up to 170°C, leading to the first plateau in the temperature range 180—200°C. X-Ray examination indicated that $(NH_4)_2O \cdot 3\ MoO_3$ was formed at this step, and not $(NH_4)_2O \cdot 2.5\ MoO_3$ as previously described for sample I. The second step starts at 210—230°C, corresponding to $(NH_4)_2O \cdot 4\ MoO_3$, as with sample I. It is interesting to show that the weight change in the second step in sample I is markedly steeper, having nearly double the weight loss as compared with sample II.

Schwing-Weill [7] and Louisy and Dunoyer [12] suggested that on heating, the compounds 3 $(NH_4)_2O \cdot 7\ MoO_3 \cdot x\ H_2O$ passed a long, wide composition range. The difference in behaviour between the two samples may be attributed to the difference in the composition of the starting material.

Isothermal study

At this stage of the present investigation it is difficult to exclude the formation of $(NH_4)_2O \cdot 12\ MoO_3$ observed by Schwing-Weill [7] and $(NH_4)_2O \cdot$

TABLE 2

X-Ray data of the intermediate decomposition products of ammonium heptamolybdate

Intermediate (formation conditions)	Present work		Schwing—Weill [7]		Hegedus and co-workers [10]		ASTM	
	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
$(NH_4)_2O \cdot 2.5\ MoO_3$	6.62	100	6.602	s	6.61	100		
(Sample I, 110°C, 30 min)	5.27	70	5.254	w	5.26	20		
	3.98	40	4.07	s	4.10	50		
	3.45	40	3.44	s	3.451	80		
	2.90	65	2.904	m	2.919	30		
$(NH_4)_2O \cdot 3\ MoO_3$	6.82	100	6.92	s				
(Sample II, 110°C, 2 h;	5.28	70	5.298	s				
180°C, 30 min)	3.90	40	3.92	s				
	3.45	50	3.46	m				
	3.30	40	3.31	m				
	2.96	40	2.95	m				
$(NH_4)_2O \cdot 4\ MoO_3$	9.14	88	9.167	s	9.6	80		
(Sample I, 180°C, 1 h;	7.15	100	7.166	s	7.2	30		

(Sample II, 180°C, 2 h;	4.76	45	4.776	m	4.8	10		
205°C, 30 min)	3.56	70	3.578	m	3.59	20		
	3.30	45	3.29	w	3.30	100		
	2;93	70	2.934	s				
$(NH_4)_2O \cdot 12\,MoO_3$ [7] or	4.77	22	4.548	m	4.585	25		
$(NH_4)_2O \cdot 14MoO_3$ [10]	3.24	100	3.429	s	3.462	100		
(Sample I or II, 240°C,	3.031	25	3.025	s	3.046	70		
80 min)	2.937	35	2.879	w	2.889	3		
	2.649	20	2.625	w	2.641	5		
	1.843	20	1.849	s	1.862	30		
$(NH_4)_2O \cdot 22\,MoO_3$	3.25	100			3.053	70		
(Sample I or II, 260°C,	3.477	60			3.483	60		
1 h)	2.653	25			2.653	5		
	2.527	22			2.543	60		
	1.951	10			1.955	10		
	1.849	20			1.862	30		
$MoO_3 \cdot xH_2O$	6.983	64					6.93	34
(Sample I, 280°C, 1 h)	3.818	68					3.81	82
MoO_3 (Sample II, 310°C, 1 h;	3.24	100					3.26	100
350°C, 1 h)	2.657	32					2.655	35
	2.312	45					2.309	31

TABLE 3

The IR absorption peaks (cm^{-1}) of ammonium heptamolybdate at its intermediate decomposition products

$3(NH_4)_2O \cdot 7\ MoO_3 \cdot 4\ H_2O$ (sample I)	$(NH_4)_2O \cdot 2.5\ MoO_3$ (I, 110°C, 30 min)	$3(NH_4)_2O \cdot 7\ MoO_3 \cdot H_2O$ (sample II)	$(NH_4)_2O \cdot 3\ MoO_3$ (II, 110°C, 2 h)	$(NH_4)_2O \cdot 4\ MoO_3$		$(NH_4)_2O$ 12 MoO_3 $(NH_4)_2O$ 14 MoO_3, (I or II, 240°C, 80 min)
				(II, 180°C, 2 h)	(II, 205°C, 30 min)	
307	308	310				
364	360	355				
395	390	395				
			435	430	430	
470	480	480	470	470	475	470
				525	520	520
			555	550	550	
570		570		575	575	575
	630			625	625	625
635						
655	655	650				
	690	685				
			730			
	740					
					755	
				760		
		775				
	798					
						825
840		840				
	855	855				
			866		866	866
880	880			880		
890	895		895			895
			908	910	910	
920		918				
	930			925	925	
	940	945				
			950	955	950	950
						999
1400	1410	1420	1410	1420	1420	1410
1630						
1640					1640	1645
	1655	1655	1655	1650		
1680		1665				
				2290	2280	
	2320			2320	2320	2325
2340		2340	2330			
2810	2800					

$(NH_4)_2O \cdot 22\,MoO_3$ (I or II, 260°C, 1 h)	$MoO_3 \cdot x\,H_2O$		MoO_3 (II, 350°C, 1 h)	
	(I, 280°C, 1 h)	(II, 310°C, 1 h)		
				Given for ammonium heptamolybdate [17]
475	475	475	480	ν OM_3 (low) [18]
				Given for ammonium heptamolybdate [17] and for MoO_3 (ν OM_3 high)
		630	630	$2\nu_1$ (307 × 2) [18]
635	640			
				Given for ammonium heptamolybdate [17]
825	830	830	830	ν OM_2 [18]
				Given for ammonium heptamolybdate [17]
875	880	880	880	ν ($Mo{-}O_3$) [18]
1000	1000	1000	1000	ν ($Mo{-}O_1$) [18]
1410				Lower frequency absorption of NH [20]. NH_4^+ ion bending vibration
1640	1640			Doubly degenerate bending ν_4 [19]
				Free H_2O
		2280	2280	MoO_3 [18]
2325	2320	2320	2320	MoO_3 [18]

TABLE 3 (continued)

$3(NH_4)_2O \cdot 7\,MoO_3 \cdot 4\,H_2O$ (sample I)	$(NH_4)_2O \cdot 2.5\,MoO_3$ (I, 110°C, 30 min)	$3(NH_4)_2O \cdot 7\,MoO_3 \cdot H_2O$ (sample II)	$(NH_4)_2O \cdot 3\,MoO_3$ (II, 110°C, 2 h)	$(NH_4)_2O \cdot 4\,MoO_3$		$(NH_4)_2O \cdot 12\,MoO_3$ $(NH_4)_2O \cdot 14\,MoO_3$ (I or II, 240°C, 80 min)
				(II, 180°C, 2 h)	(II, 205°C, 30 min)	
		2830				
			2950			
3025	3020	3025				
3180	3180	3180	3110	3100	3110	3100
3510						
				3590	3600	
						3610
				3680	3680	
						3700

14 MoO_3 and $(NH_4)_2O \cdot 22\,MoO_3$ observed by Hegedus and co-workers [10]. It is therefore deemed desirable to gain further insight into the decomposition of ammonium heptamolybdate. For this reason, the samples were subjected to heating in air at constant temperatures lying between 110 and 300° C, and the weight loss was recorded as a function of time. The intermediate compounds obtained at every stage were identified by X-ray and IR.

X-Ray analysis

The strongest diffraction lines for each intermediate product are indexed and compared with the corresponding lines of the previous authors in Table 2. A strong coincidence is observed between both $(NH_4)_2O \cdot 12\,MoO_3$ obtaned by Schwing-Weill [7] and $(NH_4)_2O \cdot 14\,MoO_3$ obtained by Hegedus and co-workers [10] and the intermediate product obtained at 240° C.

Infrared absorption

Collective IR absorption data for the starting materials and the intermediate compounds are given in Table 3. The peaks are assigned to the corresponding stretching vibration. It is observed that the peaks corresponding to NH_3 and H_2O gradually fade with increase in ignition temperature. Heating of the two samples to 110° C gave different compounds, their absorption peaks can be easily compared with $(NH_4)_2O \cdot 2.5\,MoO_3$ and the $(NH_4)_2O \cdot 3\,MoO_3$ respectively. Heating to 180—210° C for each of the two samples gave the octamolybdate $(NH_4)_2O \cdot 4\,MoO_3$. The intermediate compounds obtained from the isothermal heating at 240° C gave IR absorption peaks which are easily compared with both $(NH_4)_2O \cdot 14\,MoO_3$ given by Hegedus and co-

$(NH_4)_2O \cdot$ 22 MoO_3	$MoO_3 \cdot x\,H_2O$		MoO_3
(I or II, 260°C, 1 h)	(I, 280°C, 1 h)	(II, 310°C, 1 h)	(II, 350°C, 1 h)

			NH_3 stretching vibration [21]
			NH stretching vibration [17]
3525			2 NH_3H_2O or a weaker NH...O
		3590	
3620	3620		
		3680	ν HOH
3700			

workers [10] and $(NH_4)_2O \cdot 12\,MoO_3$ given by Schwing-Weill [13]. Heating at 260°C indicated the formation of $(NH_4)_2O \cdot 22\,MoO_3$ obtained by Hegedus and co-workers [10].

Prior to the formation of MoO_3, the IR spectrum of the solid phase at 280°C shows Mo—O stretching vibrations characteristic of MoO_3. However, at 3525 and 1640 cm^{-1}, i.e. for the ν HOH and δ HOH frequencies, respectively, a weak absorption which is not due to moisture of the KBr pellets still occurs. Accordingly, $MoO_3 \cdot x\,H_2O$ is formed. MoO_3 without OH bonds can only be prepared by long heating above 310—350° C.

It is now clear that the decomposition steps are: $(NH_4)_2O \cdot 2.5\,MoO_3$ or $(NH_4)_2O \cdot 3\,MoO_3$ (according to the water molecules in the starting material); $(NH_4)_2O \cdot 4\,MoO_3$; $(NH_4)_2O \cdot 12\,MoO_3$ or $(NH_4)_2O \cdot 14\,MoO_3$ and $(NH_4)_2O \cdot 22\,MoO_3$. It is not easy to differentiate between $(NH_4)_2O \cdot 12\,MoO_3$ and $(NH_4)_2O \cdot 14\,MoO_3$, firstly because the X-ray and IR data obtained by both Schwing-Weill [7,13] and Hegedus and co-workers [10] are coincident; and secondly because the weight losses accompanying the transformation of $(NH_4)_2O \cdot 4\,MoO_3$ to both $(NH_4)_2O \cdot 12\,MoO_3$ or $(NH_4)_2O \cdot 14\,MoO_3$ are approximately equal. Hegedus and co-workers [10] did not consider the previous results of Schwing-Weill [7].

The three well-defined intermediate products are $(NH_4)_2O \cdot 2.5\,MoO_3$ or $(NH_4)_2O \cdot 3\,MoO_3$ (according to the starting material); $(NH_4)_2O \cdot 4\,MoO_3$ and MoO_3 (end product). The formation of the latter phases, $(NH_4)_2O \cdot 12\,MoO_3$ or $(NH_4)_2O \cdot 14\,MoO_3$ and $(NH_4)_2O \cdot 22\,MoO_3$, occurs through relatively narrow temperature intervals. This involves rapid rearrangement of the crystal lattice after the collapse of the preceding phase. Thus conversion of $(NH_4)_2O \cdot 4\,MoO_3$ to $(NH_4)_2O \cdot 12\,MoO_3$ or $(NH_4)_2O \cdot 14\,MoO_3$ and $(NH_4)_2O \cdot 22\,MoO_3$ does not seem to be such a transformation.

CONCLUSION

According to the above results, the decomposition of ammonium heptamolybdate to MoO_3 in air proceeds as follows

$$3(NH_4)_2O \cdot 7\,MoO_3 \cdot 4\,H_2O \xrightarrow{100^\circ C} (NH_4)_2O \cdot 2.5\,MoO_3 \xrightarrow{210^\circ C} (NH_4)_2O \cdot 4\,MoO_3 \xrightarrow{240^\circ C} (NH_4)_2O \cdot 12\,MoO_3 \xrightarrow{260^\circ C} (NH_4)_2O \cdot 22\,MoO_3 \xrightarrow{280^\circ C} MoO_3 \cdot xH_2O \xrightarrow{310\text{—}350^\circ C} MoO_3\,.$$

and

$$3(NH_4)_2O \cdot 7\,MoO_3 \cdot H_2O \xrightarrow{180^\circ C} (NH_4)_2O \cdot 3\,MoO_3 \xrightarrow{210^\circ C} (NH_4)_2O \cdot 4\,MoO_3 \rightarrow \ldots$$

The variation in the decomposition intermediate steps depends on the water molecules present in the starting material, the temperature and time of heating.

The formed $(NH_4)_2O \cdot 3\,MoO_3$ is distinguished from $(NH_4)_2O \cdot 2.5\,MoO_3$ and also differs from $(NH_4)_2O \cdot 4\,MoO_3$. $(NH_4)_2O \cdot 12\,MoO_3$ and $(NH_4)_2O \cdot 14\,MoO_3$ could not be distinguished. MoO_3 can be prepared in a pure state by heating ammonium paramolybdate to 310—350° C regardless of starting material.

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