GAS CHROMATOGRAPHIC STUDIES OF THE THERMAL DECOMPOSITION OF 12-MOLYBDOPHOSPHORIC ACID AND ITS SALTS IN THE SOLID STATE

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ABSTRACT

Gas chromatographic studies on the thermal decomposition of 12-molybdophosphoric acid (PMA) and its salts with the cations K^+, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, NH_4^+, Cu^{2+} and Ag^+ in the solid state, on the basis of the temperature programmed reduction with H_2, are reported. Analysis of the evolved gas (EG) and the intermediate solid product (ISP) for the pyrolysis of the above compounds shows that they usually decompose in three or four stages over the temperature range 40–640°C. It is found experimentally that the difficulty with which both the Keggin anion (KA) undergoes thermal decomposition and Mo^{6+} in KA undergoes reduction towards Mo^0 depends on the particular cation in combination with KA. If the cation itself is more difficult to reduce, the KA and Mo^{6+} in it will likewise be stabler towards decomposition and reduction, respectively, under the experimental conditions.

INTRODUCTION

In recent years, PMA and its salts have received much attention because of their selective catalytic behaviour, and a number of studies on their redox mechanism have been published [1–6]. The thermal reduction of PMA and its salts with H_2 has already been reported by Niiyama et al. [7], but the present work, of the same type using gas chromatography, seems to be the first to appear, and indeed, some interesting results are obtained.

MATERIALS

All the compounds were prepared by a standard procedure [8] and identified by their IR spectra. The K salt was calcined at 320°C for 2 h.

EXPERIMENTAL

The experimental conditions and apparatus employed for the pyrolysis of the samples were basically the same as those described previously [9], except that the chromatographic separation column was packed with Porapak T resin with a particle size of 80–100 mesh which was kept constant at 135°C. The EG was led directly into the column at intervals of 20°C. The EG curves for all compounds were obtained as a function of temperature, as shown in Fig. 1. MoO_3 was used for comparison. The results are reproducible under the experimental conditions. For each sample, the process was stopped when a full water band appeared in the EG curves and ISP was analysed by IR and X-ray diffraction when the IR signal disappeared. IR spectra were recorded with a Shimadzu IR-440 spectrometer at room temperature in air using KBr pellets. The IR spectra of the initial PMA and its Ag salt samples, and their reduced forms during reduction by H_2, are arbitrarily chosen for discussion because the spectral shapes for other PMA
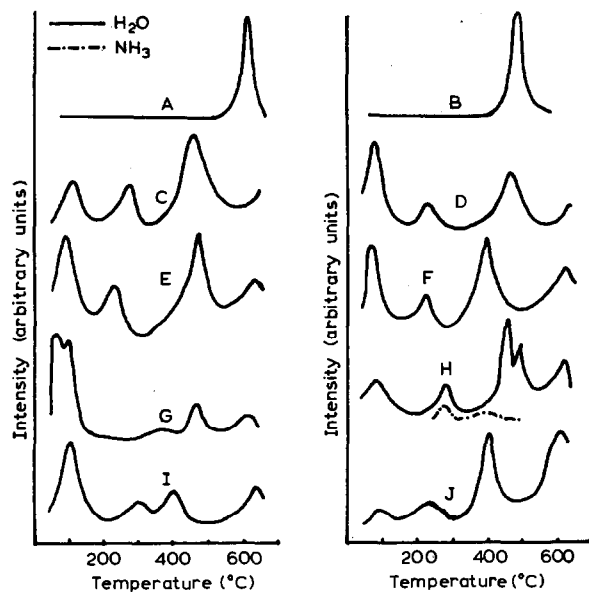

Fig. 1. EG curves for MoO (A), K salt (B), Ca salt (C), Mn salt (D), Co salt (E), Ni salt (F), PMA (G), NH_4 salt (H), Cu salt (I) and Ag salt (J) in a hydrogen atmosphere.
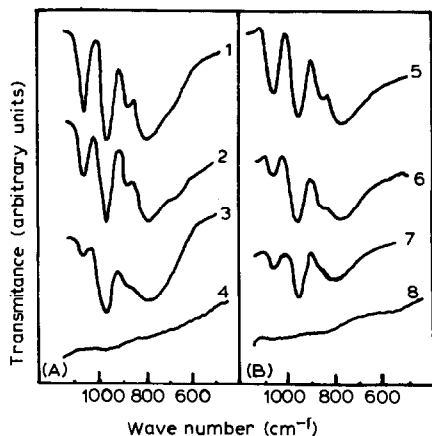
Fig. 2. IR spectra of PMA (A) and its Ag salt (B) obtained in a hydrogen atmosphere: (1, 5) initial sample; (2, 6) 160°C; (3) 400°C; (4) 500°C; (7) 290°C; (8) 450°C. Temperature of recording, 25°C.
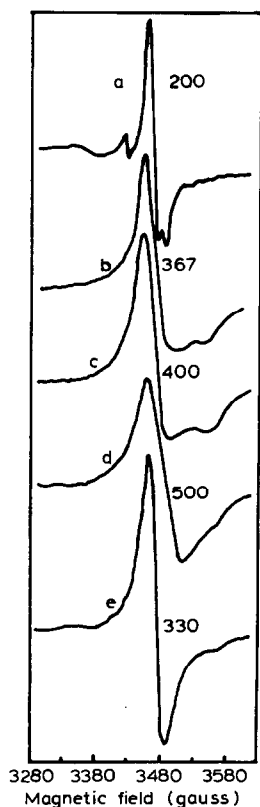

Fig. 3. ESR spectra of powdered PMA (a, b, c, d) and its K salt (e) at the temperatures (°C) indicated in the fugure. Their gains are (a) 8×10^4, (b) 6.32×10^2 (c), 5×10^2, (d) 6.3×10^3 and (e) 1.25×10^4. Temperature of recording, 110 K.

TABLE 1

X-ray diffraction analysis for ISP and the final solid products (°C)

Sample	Temp. at which ISP is taken	Corresp. phase found	Temp. at which the final solid prod. is taken	Corresp. phase found
MoO_3			640	MoO_2
K salt			580	MoO_2
Ca salt	560	MoO_2	640	MoO_2
Mn salt	540	MoO_2	640	MoO_2
Co salt	500	MoO_2	640	$MoO_2 + Mo$
Ni salt	500	MoO_2	640	$MoO_2 + Mo$
PMA	500	MoO_2 [a]	640	Mo
NH_4 salt	500	MoO_2 [a]	640	Mo
Cu salt	500	Cu [a]	640	Mo + Cu
Ag salt	450	Ag [a]	640	Mo + Ag

[a] Suboxides such as Mo_8O_{23}, $Mo_{17}O_{47}$, Mo_4O_{11}, etc. might also be produced.

salts are more or less the same if the samples are taken at corresponding reduction stages. These spectra are presented in Fig. 2.

X-ray diffraction patterns were recorded with a Shimadzu XD-3A diffractometer with Cu $K\alpha = 1.54178$ Å radiation. The corresponding phases are shown in Table 1. In addition, ESR spectra of powdered samples of PMA and its K salt under different temperatures were recorded at 110 K on a Bruker ER 200D SRC spectrometer. These spectra are given in Fig. 3.

RESULTS AND DISCUSSION

It is clear from Fig. 1 that PMA and its salts usually decompose in three or four stages in the temperature range 40–640°C with H_2, apart from the K salt which decomposes in two stages (if a hydrous sample was used). In the first stage (ca. 40–160°C), as expected, all compounds lose water of crystallization (crystalline PMA and its salts effluoresce slowly in air at room temperature, thus the amount of water of crystallization varies from sample to sample). The second stage (ca. 160–300°C; in the case of PMA 160–400°C) is due to the reduction of part of the 12 Mo^{6+} per Keggin unit to Mo^{5+}. The third stage (ca. 300–500°C) is ascribed to the destruction of KA. The last stage is ascribable to the formation of a fine Mo powder.

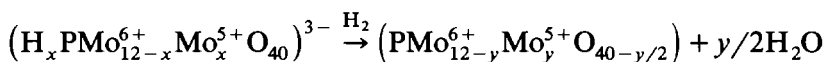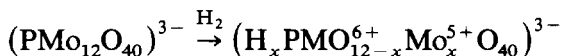*Stage I—removal of water of crystallization*

On heating, the yellow or pale-yellow compounds changed to bluish-yellow while the apple-green Ni salt and the straw-green Cu salt became bluish-green. This is probably due to the lower degree of reduction of KA at

low temperatures. The removal of crystal water was complete at about 160°C for all samples.
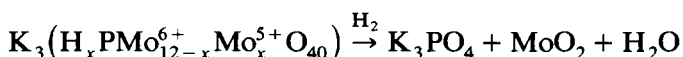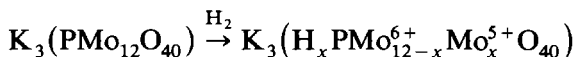
Assignment of the IR peaks due to the Keggin structure was made by Rocchiccloli-Deltcheff et al. [10]. The fully oxidized sample (see 1 and 5 in Fig. 2) shows the IR bands corresponding to three bonding types of oxygen, i.e., O bonded to the central P atom (Op band, $\nu_{Op} = 1065$ cm^{-1}; the subscript used here indicates the type of oxygen), O bonded to a single Mo atom (Ot band, $\nu_{Ot} = 960$ cm^{-1}) and O bonded to two Mo atoms (Ob band, $\nu_O = 800$ and 870 cm^{-1}). The IR spectrum of an anhydrous sample was not appreciably different to that of the hydrous one (see 2 and 6 in Fig. 2).

Stage II—partial reduction of KA

At this stage the bluish colour of the anhydrous sample, which developed at an early stage, deepened and, indeed, molybdenum blue was formed. The IR vibration at frequencies characteristic of KA did not disappear, but the intensities of the peaks due to Op, Ob and Ot bands all decreased appreciably. This is due to the conversion of part of 12 Mo^{6+} per KA to Mo^{5+} by H$_2$. ESR spectra of PMA at 200°C in Fig. 3 indicate that PMA did undergo a certain degree of reduction at low temperatures. Furthermore, there was a temperature interval between the first water bands in the EG curve for PMA in Fig. 1, i.e., water was not released over the temperature range 160–300°C. On the basis of the present findings, it is suggested that reduction of KA by H$_2$ followed a two-step mechanism, a path similar to that proposed by Katamura et al. [3]:

$$(PMo_{12}O_{40})^{3-} \xrightarrow{H_2} \left(H_x PMO^{6+}_{12-x} Mo^{5+}_x O_{40}\right)^{3-}$$

$$\left(H_x PMo^{6+}_{12-x} Mo^{5+}_x O_{40}\right)^{3-} \xrightarrow{H_2} \left(PMo^{6+}_{12-y} Mo^{5+}_y O_{40-y/2}\right) + y/2H_2O$$

The first step could be described as a hydrogen-uptake reduction process and the second one an oxygen-elimination reduction process. This was the case for PMA and most of its salts. Comparison of the EG curves of the K salt and MoO$_3$ in Fig. 1, together with the consideration of the detectable final solid product MoO$_2$, led to the suggestion that their reduction mechanism by H$_2$ should be the same, i.e., a one-step reduction. However, the situation was more complicated that expected. The ESR spectrum for the K salt at 330°C in Fig. 3 provided evidence that Mo^{6+} in KA passed into a mixed-valence state of Mo^{6+} and Mo^{5+}. Thus, the path of reduction of the K salt was proposed as follows:

$$K_3(PMo_{12}O_{40}) \xrightarrow{H_2} K_3\left(H_x PMo^{6+}_{12-x} Mo^{5+}_x O_{40}\right)$$

$$K_3\left(H_x PMo^{6+}_{12-x} Mo^{5+}_x O_{40}\right) \xrightarrow{H_2} K_3PO_4 + MoO_2 + H_2O$$

It was believed qualitatively that Ob was more active [2,3], being the type of oxygen lost in the case of PMA and its salts [3], excluding the K salt, although fast exchange of Ob and Ot in the solid state occurred [1,2]. It could be seen from the fact the two IR bands at 800 and 870 cm^{-1}, characteristic of Mo–O–Mo vibration, broadened and overlapped. The lost oxygen created a Keggin structure defect right on its site and led to the deterioration of the T_d symmetry of KA. The P–O bond is sensitive to structure symmetry while the Mo–O bond is not [6]; therefore, the IR band at 1065 cm^{-1} changed much more drastically than that at 960 cm^{-1}. If the cation is easily reduced, the corresponding metal will be obtained at this stage; thus, Cu and Ag were produced in preference to the complete destruction of KA. As for the ammonium salt, ammonia was evolved in addition to water. The evolution of ammonia gas began at 260°C and ended at about 500°C, two peak maxima being observed.

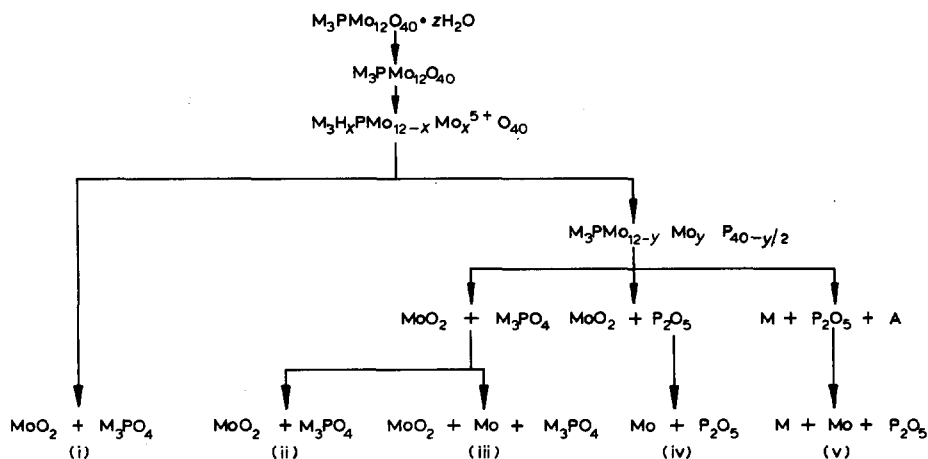*Stage III—destruction of Keggin structure*

At this stage, the solid phase for all samples became almost brown-black in colour. The IR spectra of ISP lost characteristics describing the Keggin structure. X-ray analysis of ISP shows that monoclinic MoO_2 was detected in all cases, except for Cu and Ag salts in which only metallic Cu and Ag were confirmed, respectively (the Ag salt, during preparation, was already partially decomposed). Thus, further reduction of Mo^{6+} and Mo^{5+} to Mo^{4+} led to the destruction of the Keggin structure. In what kind of state Mo in Cu and Ag salts appeared at this stage was unclear.

Stage IV—formation of powdered metallic Mo

The colour of the solid phase at this stage became black. No information was obtained for the final solid product by IR analysis, and X-ray diffraction analysis confirmed that a fine Mo powder was formed in the case of PMA, NH_4, Cu and Ag salts. It formed a mixture with the last two cation metals. In the case of Ca and Mn salts, MoO_2 remained unchanged (in a separate experiment, a mixture of Mo and MoO_2 was obtained at 700°C for the Ca salt), and in the case of Co and Ni salts, Mo was mixed with MoO_2.

From the above discussion, a general scheme (see Scheme 1) for the process of thermal decomposition of PMA and its salts with H_2 can be estimated, if the gas product is not taken into consideration. Here A stands for an unknown phase and M is the counter-cation combined with KA. Reduction schemes are suggested for (i) K, (ii) Ca and Mn, (iii) Co and Ni, (iv) PMA and NH_4 and (v) Cu and Ag salts.

Qualitative analysis of the solid product obtained in stages III and IV shows that phosphorus, the valence state of which was unchanged during reduction [6], remained in all the samples and K, Ca, Mn, Co and Ni were

$$M_3PMo_{12}O_{40} \cdot zH_2O$$
$$\downarrow$$
$$M_3PMo_{12}O_{40}$$
$$\downarrow$$
$$M_3H_xPMo_{12-x}Mo_x^{5+}O_{40}$$

$$M_3PMo_{12-y}Mo_yP_{40-y/2}$$

$$MoO_2 + M_3PO_4 \qquad MoO_2 + P_2O_5 \qquad M + P_2O_5 + A$$

$$\begin{array}{ccccc}
MoO_2 + M_3PO_4 & MoO_2 + M_3PO_4 & MoO_2 + Mo + M_3PO_4 & Mo + P_2O_5 & M + Mo + P_2O_5 \\
(i) & (ii) & (iii) & (iv) & (v)
\end{array}$$

Scheme 1.

detected in the corresponding salt samples. It was believed that the valence state of the above elements would not change during the whole process of reduction. The reason why the compounds in which the above elements ocurred showed no specific X-ray diffraction patterns was either that their quantity was small (less than 5% by weight) or they probably existed in the form of amorphous inorganic phosphates.

ESR spectra of the initial PMA and its ISP and final solid product (see Fig. 3) provide more evidence, although not conclusive, for the scheme of PMA reduction by H_2 proposed above. Both the initial and final solid product had no ESR signal. This is in reasonable agreement with the fact that Mo in the former case is in a fully oxidized form and in the latter case in a powdered elementry form. The ESR spectrum of PMA at 200°C indicates the existence of Mo^{5+}. When the temperature was raised, the ESR signal of ISP gradually became stronger and stronger. A stronger ESR signal suggests that Mo^{5+} is more populated at the corresponding temperature. At 500°C, the ESR spectrum for ISP shows the oxides, in which Mo^{5+} may still exist together with MoO_2, but further investigation is needed to elucide it. g values listed in Table 2 for the spectra of PMA at 200, 367, 400 and 500°C

TABLE 2

g values for the ESR spectrum of PMA at (a) 200, (b) 367, (c) 400 and (d) 500°C (Fig. 3)

	a	b	c	d
$g_\perp$	1.9395	1.9358	1.9308	1.9230
$g_{\parallel}$	1.9120	1.8313	1.8293	1.8351

show that the sample gradually became anisotropic, indicating the lowering of sample symmetry with the progress of reduction.

CONCLUSIONS

From the above discussion we conclude:

(1) It can be seen from Fig. 1 and Table 1 that PMA and its salts generally decompose at ca. 500°C in a hydrogen atmosphere. If the counter-cation, such as K, Ca and Mn, is more active or comparatively active, the decomposition temperature of KA will be higher than 500°C and vice versa.

(2) From Table 1 it is obvious that the thermal stability of Mo^{6+} in KA with respect to Mo^0 in H_2 depends solely on the particular counter-cation combined with KA. The situation can be roughly divided into four categories:

(a) When the counter-cation is very active or comparatively active, the product will be MoO_2 in the experimental temperature range. This is the case for K, Ca and Mn salts

(b) If the counter-cation, such as Co and Ni, is moderately active, the final product will be a mixture of Mo and MoO_2.

(c) In the case of PMA and its NH_4 salt, Mo will be obtained and the counter-cation will occur in the gas product.

(d) If the counter-cation is passive, it will form the product in addition to Mo.

Thus, an order of tendency for Mo^{6+} in KA towards Mo^0 may be suggested as follows: $K_3KA < Ca_3(KA)_2 < Mn_3(KA)_2 < Co_3(KA)_2 \leqslant Ni_3(KA)_2 < PMA = (NH_4)_3KA < Cu_3(KA)_2 < Ag_3KA$. This order parallels that of the electrochemical series of elements shown in Table 3. In summary, the counter-cation of KA was a very strong influence on the thermal reduction of Mo^{6+} towards Mo^0 in a hydrogen atmosphere.

(3) In the process of thermal decomposition of PMA and its salts with H_2 up to 640°C, Mo^{6+} passes through the mixed-valence state of Mo^{6+} and Mo^{5+}, and then becomes MoO_2 and finally a fine Mo powder. This is in

TABLE 3

Electrochemical series

Electrode couple	K^+/K	Ca^{2+}/Ca	Mn^{2+}/Mn	Co^{2+}/Co	Ni^{2+}/Ni	H^+/H_2	Cu^{2+}/Cu	Ag^+/Ag
Standard reduction Potential (V)	−2.924	−2.76	−1.029	−0.28	−0.23	0.0000	+0.3402	+0.7996

contrast to their behaviour under a nitrogen atmosphere. In addition, under the same conditions MoO_3 can only be reduced to MoO_2 by H_2. Therefore, converting Mo^{6+} into metallic Mo from either PMA or its NH_4 salt would be energetically more favourable than from MoO_3.

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