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Thermal features and behaviour of some heptamolybdates of mononitrogen aliphatic bases

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Abstract

The thermal behaviour of heptamolybdates of *n*-alkylammonium with general formula $[(C_nH_{2n+1})NH_3][Mo_7O_{24}]\cdot 3H_2O$, where $n = 4$–6, has been studied by thermoanalytical methods (DTA, TG and DTG) under argon–oxygen and argon atmospheres. It has been found that the surrounding atmosphere is an important factor which significantly influences the course of the decomposition reaction as well as the final product. In the presence of oxygen all the compounds undergo decomposition upon heating, leading to MoO_3 above 520°C. Thermogravimetric curves indicate that compounds decompose in a great number of stages and the pathway is not simple, therefore only the whole process can be described. The thermal behaviour in an inert argon atmosphere is quite different and the final solid residues at 600°C contain carbon. The essential thermal characteristics, as well as the influence of the crystal structure of the alkylammonium heptamolybdates on their thermal behaviour are also reviewed and discussed.

INTRODUCTION

Polyoxometallates have been known for well over a century [1–3], yet it has been only in the last few years that scientific interest in these materials has begun to increase dramatically [4,5]. Two reasons for the recent surge in the popularity of polyoxomolybdate chemistry are that only recently have many potential applications for these materials become well defined and has the analytical methodology for adequately characterising these complex molecules become well developed. Molybdenum oxides, and polyoxometallates in general, are extensively used as catalysts in a variety of commercially important chemical processes [6]. These catalysts are normally prepared by means of thermal decomposition of molybdates previously deposited on the catalyst carriers. Therefore, the thermal properties of polyoxometallates are very important because different thermal decompositions may lead to different metallic oxides and their properties may be

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useful to support other metals or improve the efficiency of oxidative processes catalysed by other metal oxides. Polymolybdates themselves may be used as catalysts in oxidative processes supported on alumina or silica [7]. Interest in these compounds has been renewed by increasing attempts to explore the interactions between organic substrates and catalytic metal oxide surfaces [8,9] and also owing to their photochemical properties in the photooxidation processes of organic compounds [6,10–12]. Recent studies have revealed that certain polyoxomolybdates of alkylammonium exhibit a potent antitumour activity in vitro and in vivo [13,14]. However, nitrogen organic bases commonly appear in biological systems either in neat form or as part of a macromolecule. Owing to the presence of a lone electron pair at the nitrogen atoms, these compounds can interact, in condensed phases, with Lewis or Brönsted acid, forming acid adducts or salt-type derivatives. In biological systems, nitrogen bases often occur in protonated forms that markedly influence their behaviour. Therefore, the thorough examination of the features of compounds containing protonated forms of nitrogen bases may shed more light on the behaviour of these derivatives in biological systems [15,16]. In contrast, salts of nitrogen bases are one of the simplest derivatives containing highly unsymmetrical cations. The examination of such derivatives therefore creates an opportunity to reveal the influence of the structure of a cation on the features of the appropriate salts.

In this context, and during the course of our general research programme on thermal behaviour of organoammonium polyoxometallates [17,18], we decided to study the thermal properties and thermochemistry of some *n*-alkylammonium heptamolybdates by means of techniques such as TG, DTG and DTA in order to carry out more complete characterisation of these types of compounds, in addition to other extensively used techniques such as IR and NMR spectroscopies, and to reveal the influence of the structure of a cation on the thermal features of the appropriate salts. Such thermal studies may also be of some practical importance to relate composition and structure with those properties suitable for various catalytic and biomedical applications. In this paper the essential thermal characteristics, as well as the possible influence of crystal packing on the thermal behaviour of alkylammonium heptamolybdates are reported. Three heptamolybdates of *n*-alkylammonium have been studied: hexakis(*n*-butylammonium) heptamolybdate(VI) trihydrate (BUTMO7), hexakis(*n*-pentylammonium) heptamolybdate(VI) trihydrate (PENTMO7), and hexakis(*n*-hexylammonium) heptamolybdate(VI) trihydrate (HEXMO7).

EXPERIMENTAL

Molybdenum trioxide and alkylamine bases were purchased from Merck and were used without further purification. The compounds were obtained by direct reaction between anhydrous molybdenum trioxide and the corresponding alkylamine base in aqueous solution as described in a previous paper [19]. The chemical characterisation (IR and elemental analysis) and crystal structures of these compounds were reported in the same reference.

Thermal studies were carried out under argon and argon–oxygen (4 : 1) atmospheres from room temperature to 600°C. Thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) were performed on a Setaram TAG 24 S 16 simultaneous thermal analyser at a heating rate of 5 deg min^{-1}. All thermal analysis runs were recorded in a dynamic atmosphere with a flow rate of 40 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. An amount of sample (10–20 mg) was exactly weighed in the platinum crucible. The thermally inert reference was 15 mg of α-Al_2O_3 previously calcinated at 1300°C for 5 h.

RESULTS AND DISCUSSION

Figure 1 gives the TG and DTA curves for all the heptamolybdates described in this work under an argon–oxygen atmosphere. The main features of the thermograms of all compounds are quite similar, leading to a residual mass equal to that expected for MoO_3 when the process is carried out in this atmosphere. The TG and DTG curves show that the decomposition process proceeds essentially in eight steps for BUTMO7 and seven for PENTMO7 and HEXMO7. All DTG peaks have their parallel DTA peaks. In all compounds, DTA indicates the presence of a first small endothermic peak between approximately 65 and 120°C, corresponding to the loss of three water molecules. However, in BUTMO7 the dehydration step is overlapped with the next decomposition step and this prevents accurate determination of the final dehydration step temperature.

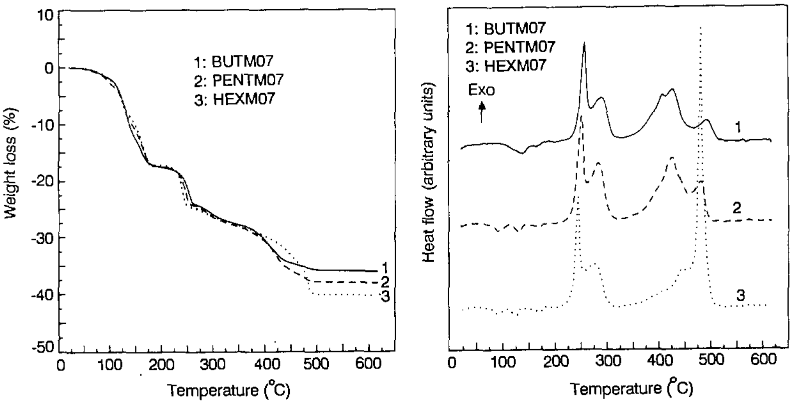

Fig. 1. TG (left) and DTA (right) curves for the thermal decomposition of the compounds BUTMO7, PENTMO7 and HEXMO7 in an argon–oxygen atmosphere.

TABLE 1

Steps, initial and final temperature (°C), partial and total mass loss, enthalpy and maximum peak for each step in the thermal decomposition of compounds in an argon–oxygen atmosphere

T_i	T_f	T_m	ΔH	Δm (%)	$\Sigma\Delta m$ (%) [a]
BUTMO7					
70	155	136	endo	11.82	
155	187	164	endo	3.67	
226	268	258	exo	5.98	
268	327	288	exo	2.96	
365	413	406	exo	3.71	
413	466	426	exo	3.10	
466	522	492	exo	0.82	36.10 (35.72)
PENTMO7					
65	112	94	endo	3.48	
112	145	131	endo	6.08	
145	191	170	endo	7.14	
220	264	252	exo	6.54	
264	322	283	exo	2.98	
370	458	425	exo	7.44	
458	502	481	exo	1.61	38.18 (38.50)
HEXMO7					
60	105	87	endo	3.10	
107	136	126	endo	4.52	
150	183	170	endo	7.13	
219	256	245	exo	6.92	
256	318	274	exo	2.43	
421	456	444	exo	2.93	
456	517	482	exo	6.27	41.08 (41.47)

[a] Calculated values for MoO_3 as final product are shown in parentheses.

The DTG peaks of dehydration are not symmetrical, and the corresponding DTA peaks are broad, which indicates that the water molecules are not isoenergetically bound, and are lost by different overlapping processes. The thermal decomposition is continued with two endothermic steps below 190°C, corresponding to mass losses observed in the TG curves. After this temperature, overlapped exothermic steps take place which could be due to the occurrence of unresolved oxidation processes. A constant mass is achieved above 520°C. The last observed solid product was identified by its X-ray powder diffraction pattern and IR spectra as MoO_3 for all the compounds. Table 1 lists steps, initial and final temperature (°C), partial and total mass loss, enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decomposition of the compounds in the argon–oxygen atmosphere. However, because most of the stages are almost overlapping, isolation of the intermediate products was difficult. Attempts to correlate the results with the theoretical mass losses were not successful, except for the final solid product.

It is interesting to note that the dehydration step gets longer as the *n*-alkylamine has one methylene group less, the final temperature being 118°C, 108°C and 99°C for BUTMO7, PENTMO7 and HEXMO7, respectively. A possible explanation of this shift towards higher temperatures can be ascribed to the different interactions of water molecules in the crystal lattice. It is well known [20,21] that polyoxomolybdate lattices exhibit extended three-dimensional networks of hydrogen-bonding interactions which stabilise the crystal structures. Water molecules participate in these networks interacting via hydrogen bonding with oxygen atoms from the polyanions and nitrogen atoms from the cations and playing an important role in the stability of crystal structure. Compounds BUTMO7, PENTMO7 and HEXMO7 crystallise in the monoclinic system, space group $P2_1/n$ and all of them are isostructural. In their crystal structures [19], the *n*-alkylammonium cations occupy the space between layers of polyanions with their N–H groups making hydrogen contacts with the oxygen atoms from polyanions and water molecules, and the hydrophobic groups leading to the holes left between these layers, along the [010] direction. According to this, the *b* parameter increases from BUTMO7 to HEXMO7 ($b_{\mathrm{BUTMO7}} < b_{\mathrm{PENTMO7}} < b_{\mathrm{HEXMO7}}$) and this effect leads to lower density values and less effective crystal packing. Water molecules also interact with oxygen atoms of polyanions, but there are not any interactions of type $O_w\text{–}H_w \cdots O_w$ between water molecules. A consequence of all this is that the water molecules' hydrogen contacts are weakened as result of the organic chain length increase, and the dehydration step temperature range is shifted towards lower temperatures. The comparison of the characteristic dehydration temperatures of several organoammonium heptamolybdates is of interest (Table 2).

Alkylammonium heptamolybdates have lower density values and lose the water molecules at lower temperature than do other heptamolybdate compounds. An increase in the density of compounds implies an increase

TABLE 2

Density values (g cm^{-3}) and dehydration step temperature ranges (°C) of some organoammonium heptamolybdate compounds

Compound	Cation	D_x	$T_i - T_f$	Reference
$(C_6H_{16}N)_6[Mo_7O_{24}]\cdot 3H_2O$	*n*-Hexylammonium	1.69	60–105	This work
$(C_5H_{14}N)_6[Mo_7O_{24}]\cdot 3H_2O$	*n*-Pentylammonium	1.77	65–112	This work
$(C_4H_{12}N)_6[Mo_7O_{24}]\cdot 3H_2O$	*n*-Butylammonium	1.91	70–118 [a]	This work
$(C_5H_7N_2)_6[Mo_7O_{24}]\cdot 6H_2O$	4-Aminopyridinium	2.17	70–113	22
$(C_5H_7N_2)_6[Mo_7O_{24}]\cdot 3H_2O$	2-Aminopyridinium	2.16	80–133	22
$(C_4H_{16}N_3)_2[Mo_7O_{24}]\cdot 4H_2O$	Diethylenetriammonium	2.68	120–180	23
$(C_4H_{16}N_3)_2[Mo_7O_{24}]\cdot 4H_2O$	Diethylenetriammonium	2.75	123–190	23

[a] This step is overlapped with the following one.

in the dehydration step range temperature. Thermoanalytical data indicate that temperature limits for the dehydration step show some dependence on the compound density and there is a shift towards higher temperature values in the denser crystal structures. This effect is clearly illustrated in the two polymorphs of bis(diethylenetriammonium) heptamolybdate(VI) tetrahydrate [23]. Both compounds have the highest density values and their water molecules are lost between 120 and 190°C. The dehydration step of the densest one finishes at a temperature that is 10°C higher than that of the other polymorph. In both crystal lattices, the water molecules also form very strong hydrogen contacts of type $N–H\cdots O_w$ and $O_w–H_w\cdots O$ as well as important contacts of the type $O_w–H_w\cdots O_w$ which are not present in the crystal structure of alkylammonium heptamolybdates. Their thermal stability is increased by the existence of additional $C–H\cdots O$ [24] contacts which are not possible in alkylammonium compounds due to the high thermal motion of chain cations. However the hydrogen contacts network is markedly different in both polymorphs, because there are more hydrogen contacts in the crystal structure of the densest compound, in which all N–H groups of two diethylenetriammonium cations take part, and the water molecules form a greater number of contacts. This produces a higher thermal stability of this compound and a quite different crystal packing in both structures.

In an argon–oxygen atmosphere, thermal decomposition for the dehydration process can be expressed by reaction (1). It is supposed that anhydrous heptamolybdates are decomposed as shown by reaction (2) and unidentified organic intermediate compounds are oxidised between dehydration step and 500°C as shown in reaction (3).

$$(HB)_6[Mo_7O_{24}]\cdot 3H_2O \xrightarrow{[O],\,\Delta} (HB)_6[Mo_7O_{24}] + 3H_2O \tag{1}$$

$$(HB)_6[Mo_7O_{24}] \xrightarrow{[O],\,\Delta} 7MoO_3 + 6B + H_2O \tag{2}$$

$$B \xrightarrow{[O],\,\Delta} NO_x + CO_2 + H_2O \tag{3}$$

In order to study possible differences in the thermal behaviour of alkylammonium heptamolybdates, decomposition in inert argon atmosphere was performed. TG and DTA curves for the decomposition of compounds in argon atmosphere are shown in Fig. 2. Thermoanalytical data are presented in Table 3. Thermal decompositions have a significant dependence on the surrounding atmosphere and all thermograms are essentially of the same pattern but are different to those in an oxidative atmosphere. Thermal decomposition in an inert atmosphere leads to a smaller number of steps. The loss of water molecules takes place between similar temperature ranges to those for oxygen atmosphere. Dehydration steps are followed by three or four endothermic processes and a progressive mass loss without clear peaks in the DTG and DTA curves. In this atmosphere, there are no exothermic peaks in the DTA curve. In argon

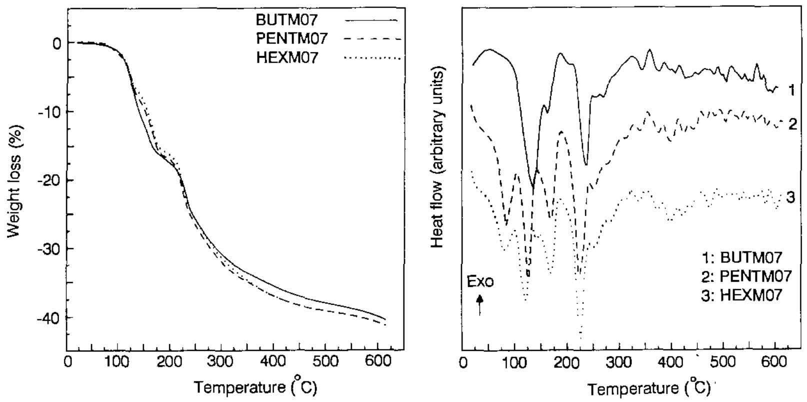

Fig. 2. TG (left) and DTA (right) for the thermal decomposition of the compounds BUTMO7, PENTMO7 and HEXMO7 in an argon atmosphere.

atmosphere, the decomposition is progressive and does not reach a constant mass in the operational temperature field.

At 600°C total mass losses are far higher than those expected for the final product molybdenum trioxide. There seem to be uncertainties about the stoichiometry of this residue. Some authors have suggested [25–27] that the catalytic decomposition of NH_3 on the surface of MoO_3 could cause some degree of reduction of MoO_3 and the final residue could be oxygen-deficient molybdenum oxide or a mixture of oxides of molybdenum(VI) and molybdenum(IV). However, Ciembroniewicz et al. [28] studied the thermal decomposition of ammonium paramolybdate in vacuo and in air or argon atmosphere. They observed substantial participation of redox reactions in the vacuum decomposition and the final product was a mixture of lower molybdenum oxides. Nevertheless, the decompositions in air or in argon atmosphere were similar and the MoO_3 obtained is only slightly reduced. In our case, elemental analyses of final black products give an indication of C presented in the composition. It is therefore possible that a product formed during the thermal decomposition of organic base could cause some reduction of trioxide of molybdenum or it could even react with oxide to give molybdenum oxocarbures or molybdenum carbures. Similar behaviour is observed in the thermal decomposition of ethylenediammonium molybdate under nitrogen atmosphere [29], where the final product was identified as a mixture of MoO_2 and Mo_2C. Cooling the thermobalance down to 400°C and reheating the sample until 600°C in oxygen, first there is an abrupt increase in mass over a short temperature range. This increase is related to occurrence of a strong exothermic peak in the DTA curve. The increase in mass continues without peaks in the DTG and DTA curve up to 600°C, at which temperature the mass of residue in the crucible was in accord with that calculated for MoO_3. The first strong exothermic process can only be explained by a metal oxidation, which releases a high amount

TABLE 3

Steps, initial and final temperature (°C), partial and total mass loss, enthalpy and maximum peak for each step in the thermal decomposition of compounds in an argon atmosphere, with ulterior oxidation from 400 to 600°C

T_i	T_f	T_m	ΔH	Δm (%)	$\Sigma\Delta m$ (%)
BUTMO7					
Argon					
65	156	136	endo	12.53	
156	192	162	endo	4.09	
195	269	236	endo	10.89	
269	600			15.09	42.60
Argon + oxygen					
400	411	403	exo	−3.34	
411	600	549	exo	−3.07	36.19
PENTMO7					
Argon					
63	108	88	endo	3.36	
108	146	131	endo	6.56	
146	190	172	endo	7.81	
190	252	226	endo	10.62	
252	600			15.45	43.80
Argon + oxygen					
400	415	404	exo	−3.51	
415	600	536	exo	−1.76	38.53
HEXMO7					
Argon					
58	99	80	endo	3.18	
99	142	125	endo	5.36	
142	190	172	endo	7.61	
190	248	228	endo	9.31	
248	600			18.54	44.00
Argon + oxygen					
400	411	404	exo	−0.99	
411	600	567	exo	−2.84	41.17

of energy at this temperature. Figure 3 shows TG and DTA curves for PENTMO7 compound using this procedure.

CONCLUDING REMARKS

Thermal decompositions of the *n*-alkylammonium heptamolybdates are complex and numerous intermediate steps take place before final products are formed. However, the dehydration steps can be identified and their temperature ranges are strongly influenced by the density values of the compounds. In general, a gradual shift towards higher temperatures is observed as the density values increase. This tendency can be explained on

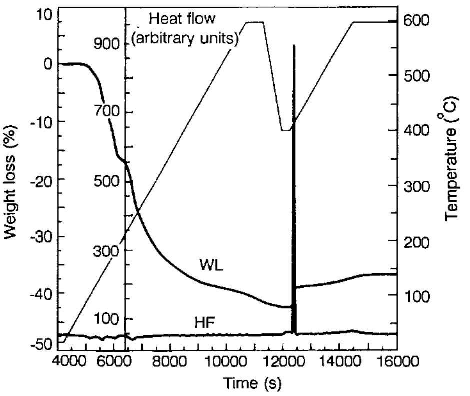

Fig. 3. Thermal decomposition of the hexakis(*n*-pentylammonium) heptamolybdate(VI) trihydrate in an argon–oxygen atmosphere (20–600°C), and ulterior oxidation from 400 to 600°C.

the basis of the different crystal packing and the interactions of water molecules in the crystal lattices.

The surrounding atmosphere significantly influences the course of the decomposition processes as well as the final products. In argon–oxygen atmosphere, the final product above 520°C is MoO_3 and this thermal method can be used for the quantitative analysis of molybdenum in this type of compound, whereas in an inert argon atmosphere the final solid products at 600°C undoubtedly contain carbon.

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