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Synthesis, solid state characterization and thermal behaviour of some *t*-butylammonium polymolybdates

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Abstract

During a study of the reaction between MoO_3 and *t*-butylamine in aqueous solution, using different amounts of reactants and pH conditions, three new polymolybdates of *t*-butylammonium were isolated: $(BH)_2[MoO_4]$ (TBUTMO1), $(BH)_6[Mo_7O_{24}] \cdot 7H_2O$ (TBUTMO7) and $(BH)_4[Mo_8O_{26}] \cdot 6H_2O$ (TBUTMO8), where B = *t*-butylamine. These compounds were characterized by means of chemical analysis and thermal and FT-IR techniques. Thermal decomposition studies were carried out using TG, DTA and DTG techniques under argon–oxygen and argon atmospheres. Final products of the thermal decompositions were analysed by elemental analysis and the X-ray powder diffraction technique. The results show that the thermal behaviour of these compounds is extremely sensitive to the presence of oxygen in the surrounding atmosphere. Under an argon–oxygen atmosphere the thermal decompositions lead to a final solid residue above 300–450°C, identified as MoO_3 by FT-IR spectral and X-ray powder diffraction data.

In an argon atmosphere, all the decomposition processes are endothermic, and the final weight losses are rather different from that expected for molybdenum trioxide. Final residues for TBUTMO1 and TBUTMO7 comprise a mixture of molybdenum(IV) oxide and amorphous compounds containing carbon. The elemental analysis of the final black X-ray amorphous product from TBUTMO8 gave an indication of carbon in its composition.

INTRODUCTION

Interest in polyoxometalates has received increasing attention in recent years because of the participation of these compounds in important industrial processes and their successful use in the biomedical field. Organoammonium polyoxomolybdates have been extensively used as precursors for the preparation of molybdenum oxides by means of thermal decomposition of polymolybdates previously deposited on catalyst carriers. Molybdenum oxides play an important role as essential components of many industrial catalysts for selective oxidation of olefins [1] and the hydrodesulphurization of oils [2]. Furthermore, isopolymolybdates are becoming interesting as

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models for the investigation of interactions between organic substrates and catalytic metal oxide surfaces [3,4], and also because of their photochemical properties in the photo-oxidation processes of organic compounds [5,6]. Recently, certain polyoxomolybdates have been recognized as being a new type of antitumour substance; in particular, some organoammonium heptamolybdates were found to exhibit potent antitumour activity in vitro and in vivo [7].

Several studies on the thermal decomposition of various heptamolybdates have demonstrated that the surrounding atmosphere and the experimental conditions play an important role in the thermal decomposition as well as the final products [8,9]. It is important to emphasize this fact not only in chemical and solid state characterization but also in the study of the thermal stability and behaviour of these compounds under different atmospheres. As different atmospheres lead to different oxides, we decided to study the thermal properties of some polymolybdates under argon–oxygen and argon atmospheres by means of techniques such as thermogravimetry (TG and DTG) and differential thermal analysis (DTA).

This paper describes the synthesis, chemical characterization and thermal properties of three new polyoxomolybdate compounds: *t*-butylammonium molybdate(VI) (TBUTMO1), hexakis(*t*-butylammonium) heptamolybdate(VI) heptahydrate (TBUTMO7), and tetrakis(*t*-butylammonium) β-octamolybdate(VI) hexahydrate (TBUTMO8).

EXPERIMENTAL

Synthesis and chemical and spectroscopic characterization of compounds

Molybdenum trioxide and *t*-butylamine ($C_4H_{11}N$) were purchased from Merck and used without further purification. Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer 240 C, H, N analyser, and molybdenum was determined thermogravimetrically as MoO_3 after thermal decomposition of the samples in an argon–oxygen atmosphere. The densities were measured by flotation in $CHBr_3$–CCl_4. The IR spectra were recorded in the 4000–400 cm^{-1} range on a Nicolet 740 FT-IR spectrometer; the solid compounds were mixed with fused potassium bromide and pressed into transparent discs.

t-Butylammonium molybdate(VI), $(BH)_2[MoO_4]$ (TBUTMO1)

To a stirred aqueous suspension (50 ml) of MoO_3 (0.68 g, 4.7 mmol) was added *t*-butylamine (0.69 g, 9.4 mmol) and the mixture was heated under reflux for 4 h (reaction (1))

$$MoO_3 + 2B \xrightarrow[H_2O,\ 100°C]{pH\ 8.4} (BH)_2[MoO_4] \qquad (1)$$

The resulting colourless solution was filtered off and then allowed to stand at room temperature. After 2 weeks, colourless crystals of TBUTMO1 were obtained (yield: 0.87 g, 60%). They were filtered off, washed with water, ethanol and diethyl ether, and dried in air. Calculated values (%) for $C_8H_{24}MoN_2O_4$: C, 31.17; H, 7.85; N, 9.09; MoO_3, 46.70. Analytical results: C, 31.09; H, 7.79; N, 9.04; MoO_3, 45.78. $D_0 = 1.44(2)$ g cm^{-3}. IR (KBr, cm^{-1}): 3000s, 2905 (sh), 2890s, 2800s, 2720s, 2610s, 2530s, 2180m br, 1650 (sh), 1620m, 1540m, 1400m, 1370m, 1310w, 1225w, 915s, 850s, 775vs, 460s (s, strong; m, medium; w, weak; br, broad; sh, shoulder).

*Hexakis(*t*-butylammonium) heptamolybdate(VI) heptahydrate, $(BH)_6$-$[Mo_7O_{24}] \cdot 7H_2O$ (TBUTMO7)*

This compound was prepared by the same method as TBUTMO1 (reaction (2)), using an aqueous suspension (500 ml) of MoO_3 (4.7 g, 32.4 mmol) and *t*-butylamine (3.43 g, 46.9 mmol)

$$7MoO_3 + 6B(exc) \xrightarrow[H_2O,\ 100°C]{pH\ 5.8} (BH)_6[Mo_7O_{24}] \cdot 7H_2O \qquad (2)$$

Crystals appeared after 2 weeks (yield: 5.27 g, 70%). Calculated values (%) for $C_{24}H_{86}Mo_7N_6O_{31}$: C, 17.72, H, 5.33; N, 5.17; MoO_3, 61.87. Analytical results: C, 17.80; H, 5.33; N, 5.22; MoO_3, 61.00. $D_0 = 1.81(1)$ g cm^{-3}. IR (KBr, cm^{-1}) 3520m, 3370m, 3310m, 3200w, 3100w, 2980vs, 2920s, 2890s, 2800s, 2690m, 2580s, 2490m, 2030m, 1970w, 1950w, 1660m, 1640m, 1600m, 1500s, 1475w, 1405s, 1380s, 1300m, 1220m, 930 (sh), 920 (sh), 895vs, 870 (sh), 845s, 655s br, 580s, 545 (sh), 480m, 450m.

*Tetrakis(*t*-butylammonium) β-octamolybdate(VI) hexahydrate, $(BH)_4$-$[Mo_8O_{26}] \cdot 6H_2O$ (TBUTMO8)*

This compound was prepared following the method described before, using an aqueous suspension (100 ml) of MoO_3 (2.7 g, 18.7 mmol) and *t*-butylamine (0.69 g, 9.4 mmol) (reaction (3))

$$8MoO_3 + 4B \xrightarrow[H_2O,\ 100°C]{pH\ 3.1} (BH)_4[Mo_8O_{26}] \cdot 6H_2O \qquad (3)$$

Crystals appeared after 3 days (yield: 3.01 g, 81%). Calculated values (%) for $C_{16}H_{60}Mo_8N_4O_{32}$: C, 12.10; H, 3.81; N, 3.53; MoO_3, 72.50. Analytical results: C, 12.12; H, 3.69; N, 3.46; MoO_3, 71.95. $D_0 = 2.26(1)$ g cm^{-3}. IR (KBr, cm^{-1}) 3600s, 3540s br, 3440s, 3240s, 3100s br, 3000s, 2950m, 2900m, 2830w, 2790w, 2670w, 2500w, 2430w, 2000w, 1905w, 1640m, 1605s, 1510vs, 1405s, 1380s, 1300s, 1220m, 1090w, 960 (sh), 945vs, 935 (sh), 920s, 900vs, 850vs, 845s, 720 (sh), 700vs, 665vs, 550s, 525m, 480m, 450m, 405m.

Thermal studies

Thermal studies were carried out under argon–oxygen (4:1 v/v) and argon atmospheres from room temperature to 600°C. The TG, DTA and

DTG were performed on a Setaram TAG 24 S 16 simultaneous thermal analyser at a heating rate of 5°C min^{-1}. All thermal analysis runs were recorded in a dynamic atmosphere. An amount of sample (23–25 mg) was exactly weighed in the platinum crucible; the thermally inert reference was 20 mg of α-Al_2O_3 previously calcined at 1300°C for 6 h. The X-ray powder diffraction technique was used to identify the final products using a Philips PW 1710 instrument with Cu Kα radiation. Diffraction patterns were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards.

RESULTS AND DISCUSSION

IR spectroscopy

IR spectroscopy was a good method for identifying the type of polyanion and the presence of protonated organic cations and water molecules. The IR spectra of the compounds (Fig. 1) are very similar from 4000 to 1000 cm^{-1}, where we find the bands corresponding to cations and water molecules (for hydrated compounds), but they are substantially different in the range 1000–400 cm^{-1} where the bands corresponding to the anions are detectable, as is expected from the literature [10].

The IR spectrum of TBUTMO1 shows three bands in the range 915–775 cm^{-1}, which are assigned to Mo–O_t (t = terminal) stretching frequencies and one strong band at 460 cm^{-1} assigned to the deformation modes of the MoO_2 group. The IR spectrum of TBUTMO7 displays several bands between 930 and 895 cm^{-1} associated with the *cis*-$[Mo(O_t)_2]$ unit, and two other bands, 870 and 845 cm^{-1}, assigned to the symmetric and antisymmetric vibration of Mo–O_b (b = bridge) groups. The rest of the bands can be assigned to the breathing of the polyanion. In contrast, the IR spectrum of TBUTMO8 exhibits characteristic features of β-octamolybdate compounds and is characterized by a very strong band at 945 cm^{-1} assigned to stretching of the terminal Mo–O bonds and three other strong peaks at 920, 900 and 850 cm^{-1}, attributable to the stretching of $[Mo_2O_2]$ units. There is a strong band at 700 cm^{-1} which is characteristic for β-octamolybdate anions, but it is not present in IR spectra of heptamolybdate anions.

Thermal behaviour

Table 1 lists the steps, initial and final temperatures (°C), partial and total weight losses, enthalpy (endothermic or exothermic) and peak maximum for each step in the thermal decomposition of the compounds in the argon–oxygen atmosphere.

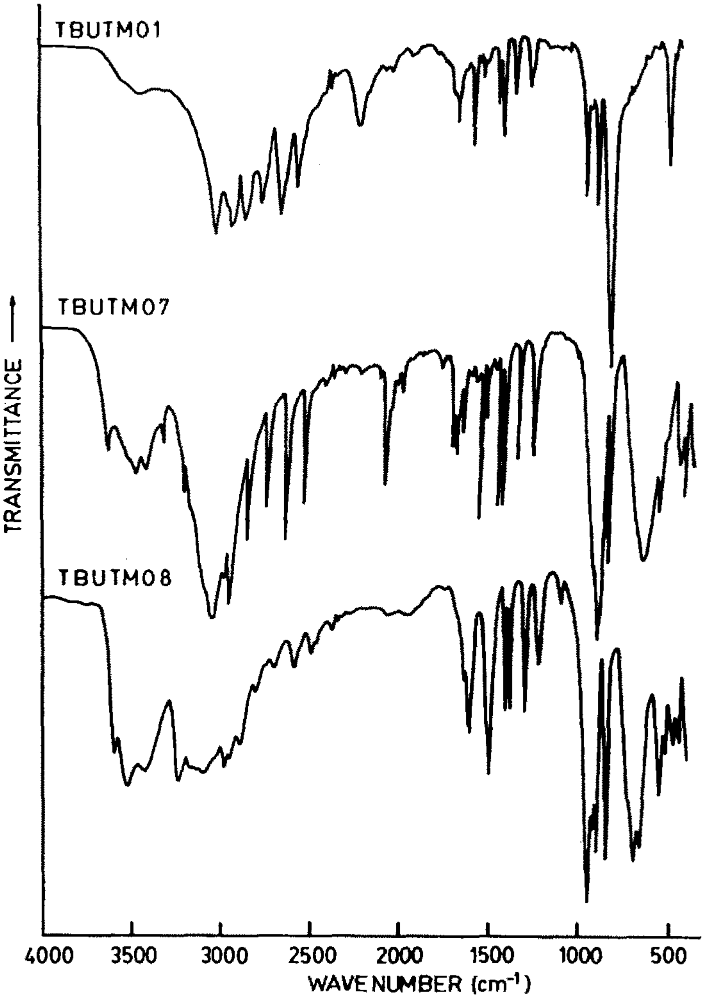

Fig. 1. FT-IR spectra of the compounds TBUTMO1, TBUTMO7 and TBUTMO8.

The thermal analysis of TBUTMO1 in an argon–oxygen atmosphere (Fig. 2) shows that the compound is anhydrous and stable up to approximately 150°C, at which a first abrupt weight loss takes place which corresponds to an endothermic peak centred at 179°C. After this stage a stable amorphous solid product was obtained. The thermal decomposition was followed by a sharp exothermic step related to the oxidation of the organic base. A constant weight was achieved above 300°C.

The two hydrated compounds, TBUTMO7 and TBUTMO8, start their decomposition above 58°C, losing their water molecules in an endothermic process (Fig. 3). The DTG peaks of the dehydration steps are not symmetrical and the DTA curve peaks are broad, indicating that the water

TABLE 1

Steps, initial and final temperature (°C), partial and total weight losses, enthalpy and peak maximum for each step in the thermal decomposition of the compounds TBUTMO1, TBUTMO7 and TBUTMO8 in an argon–oxygen atmosphere

Step	T_i	T_f	T_m	ΔH	$\%\Delta m$	$\Sigma\%\Delta m$ [a]
TBUTMO1						
1	152	201	179	Endo	35.15	
2	252	278	269	Exo	13.07	
	278	300				54.22 (53.30)
TBUTMO7						
1	58	123		Endo	6.81	
2	159	200	181	Endo	12.83	
3	250	280	269	Exo	12.11	
4	310	388	359	Exo	2.59	
	388	400				39.00 (38.13)
TBUTMO8						
1	59	160	116	Endo	6.83	
2	228	266	261	Exo	6.92	
3	266	296	289	Exo	9.65	
4	330	410	370	Exo	2.52	
	410	500				28.05 (27.50)

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

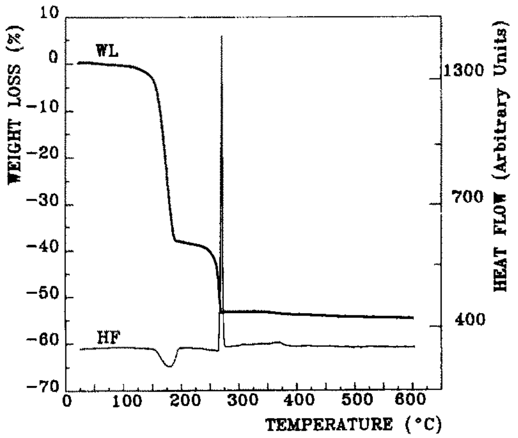

Fig. 2. TG and DTA curves for the thermal decomposition of the compound TBUTMO1 in an argon–oxygen atmosphere.

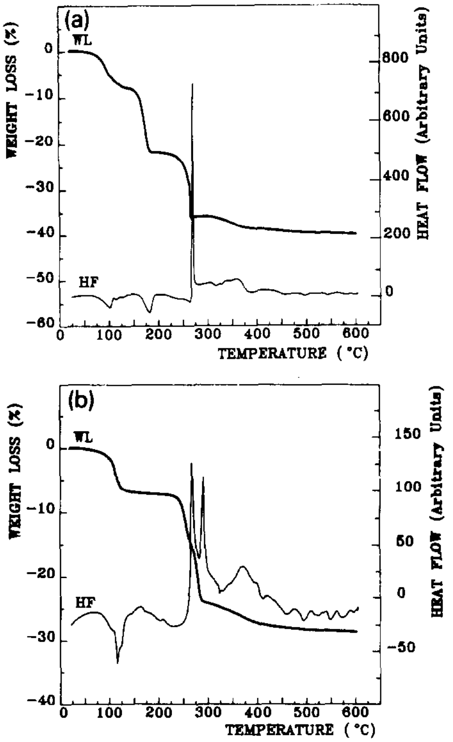

Fig. 3. TG and DTA curves for the thermal decomposition of the compounds TBUTMO7 (a) and TBUTMO8 (b) in an argon–oxygen atmosphere.

molecules are not isoenergetically bound and are lost by different overlapping steps.

The dehydration step for TBUTMO8 shows three peaks in the DTA curve, which is in accordance with the existence of three independent crystallographic water molecules in the crystal structure [11]. The dehydration processes (reaction (4)) lead to the corresponding anhydrous polymolybdate salts:

$$(BH)_4[Mo_8O_{26}] \cdot 6H_2O \xrightarrow{[O],\,\Delta} (BH)_4[Mo_8O_{26}] + 6H_2O \qquad (4)$$

Decomposition of the anhydrous TBUTMO7 follows immediately after the dehydration process with one endothermic step which leads to a stable intermediate product (200–250°C), and one exothermic step which produces another stable intermediate residue between 280–310°C. Attempts to correlate these stable intermediate products with the theoretical weight losses of complete amine molecules were not successful. After an exothermic stage, the thermal decomposition finishes at 400°C.

The stable anhydrous compound from TBUTMO8 has lost the crystalline condition, but it has been identified by IR spectra and elemental analysis. This anhydrous octamolybdate undergoes decomposition in three

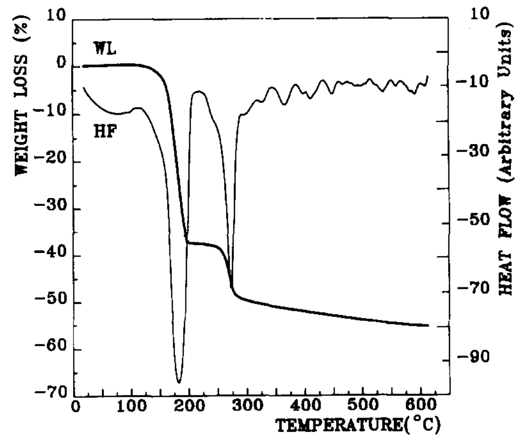

Fig. 4. TG and DTA curves for the thermal decomposition of the compound TBUTMO1 in an argon atmosphere.

overlapping exothermic stages without stable intermediate products. A constant weight is achieved above 500°C. The final stable products of the three compounds were identified by X-ray powder diffraction data and IR spectroscopy as the orthorhombic MoO_3 (ASTM 5-0508). It is supposed that anhydrous polymolybdates are decomposed as shown by reaction (5) and unidentified organic intermediate compounds are oxidized as shown in reaction (6):

$$(BH)_p[Mo_qO_{3q+p/2}] \xrightarrow{[O],\,\Delta} qMoO_3 + pB + (p/2)H_2O \tag{5}$$

$$B \xrightarrow{[O],\,\Delta} NO_x + CO_2 + H_2O \tag{6}$$

where (p, q) is (2, 1), (6, 7) or (4, 8) for TBUTMO1, TBUTMO7 and TBUTMO8 respectively.

Because of the influence of the surrounding atmosphere of polyoxometalates during their thermal decomposition [8,9,12], the thermal behaviour of the three compounds in an argon atmosphere was studied from room temperature to 600°C. Figure 4 displays the thermal decomposition of TBUTMO1 in an inert atmosphere. The TG and DTA curves for compounds TBUTMO7 and TBUTMO8 are shown in Fig. 5. The thermoanalytical data are listed in Table 2.

Thermal decompositions for the three compounds are quite different from those studied under an oxygen atmosphere. All processes are endothermic in an inert atmosphere. Decomposition of the three compounds finishes at 600°C with a weight loss different to that expected for molybdenum trioxide. X-ray powder diffraction data of the black final products from TBUTMO1 and TBUTMO7 revealed the presence of the monoclinic MoO_2 (ASTM 5-0452). No MoO_3 or other molybdenum oxide could be detected. Some authors have suggested [13–15] that the catalytic decompo-

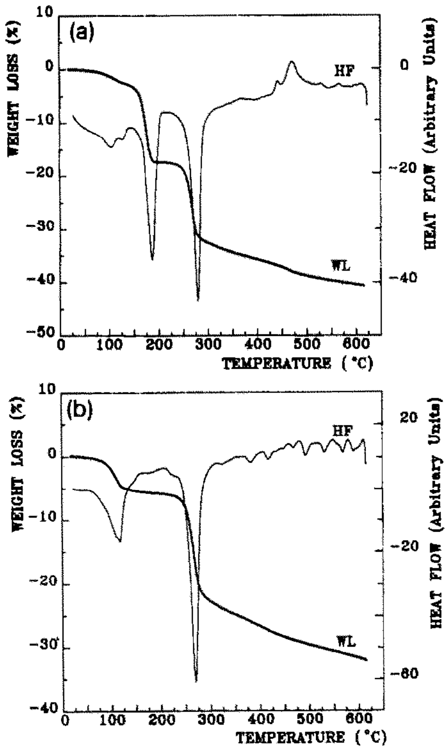

Fig. 5. TG and DTA curves for the thermal decomposition of the compounds TBUTMO7 (a) and TBUTMO8 (b) in an argon atmosphere.

TABLE 2

Thermoanalytical data for the compounds TBUTMO1, TBUTMO7 and TBUTMO8 in an argon atmosphere

Step	T_i	T_f	T_m	ΔH	$\%\Delta m$	$\Sigma\%\Delta m$
TBUTMO1						
1	151	204	183	Endo	35.94	
2	252	295	274	Endo	11.06	
3 [a]	274	600				55.53
TBUTMO7						
1 [b]	58	133	98	Endo	2.39	
	150	201	180	Endo	14.13	
2	241	293	272	Endo	14.14	
3 [a]	293	600				40.30
TBUTMO8						
1	60	160	118	Endo	6.32	
2	240	311	270	Endo	16.54	
3 [a]	340	600				31.47

[a] Progressive weight loss without clear peaks in the DTG and DTA curves.

[b] Overlapping steps.

sition of NH_3 on the surface of molybdenum(VI) oxide induces the reduction of MoO_3 to give molybdenum(IV) oxide or a mixture of molybdenum oxides. However, we cannot explain the total weight losses on the basis of the experimentally detected molybdenum(IV) oxide because the products obtained at this temperature also contain a high amount of carbon (about 4.5%). It is possible that a product formed during the thermal decomposition of the organic base could cause some degree of reduction of the oxide of molybdenum, or it could even react with it to give molybdenum oxocarbides or molybdenum carbides. A similar behaviour is observed in the thermal decomposition of ethylenediammonium molybdate under a nitrogen atmosphere [12], where the final product was identified as a mixture of MoO_2 and Mo_2C. In our case, all peaks in the X-ray powder diffraction patterns of the final products from TBUTMO1 and TBUTMO7 correspond to MoO_2; therefore the unidentified compounds containing carbon may be amorphous. The final black powder from TBUTMO8 also exhibits carbon in its composition, but the X-ray diffraction pattern does not display peaks, which indicates that the residue is amorphous.

CONCLUDING REMARKS

The reaction of MoO_3 with *t*-butylamine base in aqueous solution, using different amounts of reactants and pH conditions, yields three new molybdate salts which have been characterized by elemental analyses and thermal and spectroscopic techniques. IR spectroscopy permits the identification of not only the presence of cations and water molecules but also the type of anion in the compounds. The results indicate that the thermal decomposition of the *t*-butylammonium polyoxomolybdates, as well as the final products which are formed, are strongly influenced by the atmosphere involved and the starting compound. Whereas the thermal decompositions under an excess of oxygen lead to MoO_3 as the final solid stable product, in an inert atmosphere the organoammonium cation reduces, directly or indirectly, the molybdenum atoms of the polyanion, yielding a mixture of MoO_2 and/or carbides, which depends on the starting compound.

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