SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF 2,6- AND 3,4-DIMETHYLPYRIDINIUM AND 2,4,6-TRIMETHYLPYRIDINIUM OCTAMOLYBDATES

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2,6- and 3,4-dimethylpyridinium and 2,4,6-trimethylpyridinium octamolybdates were synthesized and characterized and their thermal decompositions were studied by means of thermogravimetry. The thermal stabilities follow the sequence: 2,4,6-TMPO < 2,6-DMPO < 3,4-DMPO, which seems to be related to the positions of the methyl groups on the pyridine ring. Kinetic parameters were calculated for the first decomposition step of the two dimethylpyridinium octamolybdates. A nucleation mechanism is proposed. The best fit corresponds to a random nucleation (one nucleus per particle) controlled equation. The calculated activation energies were 120.9 and 133.7 kJ/mol^{-1} for the 2,6- and the 3,4 derivative, respectively.

Control of the chemical reactivity of solids is one of the important current problems in solid-state chemistry [1]. The authors are continuing studies on the solid-state thermal decompositions of polymetalates of organic bases [2–6] on an elementwise basis, to establish the generalities, trends and differences, if any, by changing the cation or the anion. Some previous studies [4, 5] were concerned with the thermal decompositions of octamolybdates of pyridinium and its derivatives. The influence of the organic bases on the initial decomposition temperature was established. In the present work three new octamolybdates of other alkyl derivatives of the pyridinium cation have been synthesized. After characterization by means of elemental analysis and infrared and electronic spectroscopy, thermogravimetry was carried out to check the above-described influence and to make a systematic study of the effects of substituents at different positions of the pyridine ring on the thermal stability of the octamolybdate. The kinetic parameters for the first step of thermal decomposition of the two dimethyl derivatives were calculated via the methods of Satava [7] and Abou-Shaaban [8].

Experimental

Preparation of the compounds

The new salts 2,6-dimethylpyridinium octamolybdate (2,6-DMPO), 3,4-dimethylpyridinium octamolybdate (3,4-DMPO) and 2,4,6-trimethylpyridinium octamolybdate (2,4,6-TMPO) were synthesized via the method previously described [3, 6] for analogous compounds.

The analytical data on the three compounds (Table 1) are in agreement with the formula $(BH)_4Mo_8O_{26} \cdot nH_2O$, where B is the organic base and n is the number of molecules of crystallization water.

Table 1 Analytical data

Compound	n		%C	%N	%H	%MoO$_3$
2,6-DMPO	2	Calc.	20.34	3.39	2.66	69.72
		Exp.	20.40	3.55	2.70	69.60
3,4-DMPO	0	Calc.	20.80	3.47	2.47	71.28
		Exp.	20.90	3.52	2.41	71.50
2,4,6-TMPO	2	Calc.	22.50	3.28	3.04	67.42
		Exp.	22.65	3.25	3.05	67.87

Previous TG curves were used to determine molybdenum, and MoO_3 was obtained as final residue at 600°. These curves also indicated two moles of water of crystallization per molecule in 2,6-DMPO and 2,4,6-TMPO.

Methods

TG studies

Thermogravimetric studies were carried out on a Perkin–Elmer model TGS–1 system at a heating rate of 5 deg/min^{-1} in a nitrogen atmosphere. The amount of sample was 6–7 mg. The kinetic parameters were determined on the basis of the general kinetic relation

$$g(\alpha) = \int_0^1 \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T} K(T)\,dt \qquad (1)$$

where $K(T) = K_0 exp(-E_a/RT)$ (Arrhenius law); K_0 is the frequency or pre-exponential factor; E_a is the activation energy; and α is the mole fraction. In this

work we have used all the principal expressions of $g(\alpha)$ indicated in the literature [1] following the five physical models of solid-state chemistry: nucleation and nucleus growth, phase boundary reaction, diffusion, potential law and reaction order. Expression (1) was solved by the widely employed approximation of Satava [7].

Other determinations

The infrared spectra of the octamolybdates and organic base chlorides were obtained in potassium bromide pellets at 20° with a Perkin–Elmer 1430 spectrophotometer.

The visible/UV spectra of aqueous solutions of the compounds and base chlorides were taken with a Beckman 5260 spectrometer in the region 200–700 nm.

Results and discussion

The obtained compounds are monocrystal and colourless, apart from 2,4,6-TMPO, which is slightly green. They are poorly soluble in water and in dimethylsulphoxide and insoluble in the usual organic solvent. The crystals are non-hygroscopic and fairly stable in air.

The IR spectra exhibit characteristic bands due to the $N—H^+$, $C—H$, $C—C$ and $C—N$ bonds of the organic bases. Table 2 shows the frequencies of the main bands and their assignments [9]. The 700–1000 cm^{-1} region is characteristic of the stretching vibrations of the $Mo—O$ terminal bonds [10–12]. On the other hand, bands in the range 835–825 cm^{-1} indicating mean T_d symmetry, as in tetramolybdates or α-octamolybdates [13, 14], were not observed. Weaker bands are observed between 680–300 cm^{-1}, which are consistent with metal-oxygen bridging deformation vibrations.

The electronic spectra show an absorption maximum at 268, 256 and 266 nm for 2,6-DMPO, 3,4-DMPO and 2,4,6-TMPO, respectively, coinciding with the maximum for the three free bases. However, the bands have extinction coefficients 6 times higher than those of the unprotonated bases and twice those of the base chlorides. This is due to the protonation on the nitrogen decreasing the symmetry of the molecule and the octamolybdate anion absorption. Polymetalates exhibit charge-transfer bands (oxygen-to-metal) within the range 240–270 nm [15].
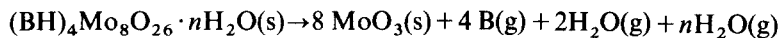
The TG curves of the three compounds are reproduced in Fig. 1. It is quite evident that 2,6-DMPO and 2,4,6-TMPO lose weight in three decomposition steps, whereas 3,4-DMPO does so in two. The first step for the compounds with water of crystallization is a loss of 2.10 and 2.09%, respectively, in the temperature range 70–115°. The observed weight losses are attributed to dehydration processes as they

Table 2 Infrared spectra (cm^{-1})

Compound			Assignments
2,6-DMPO	3,4-DMPO	2,4,6-TMPO	
3450 (m, b)	—	3600 (m, b)	v—O—H
3100 (w)	3140 (w)	3100 (m)	v—C—H ar.
2980 (w)	3095 (w)	3000 (m)	
2770 (w)	2910 (w)	2300 (w)	v—N—H$^+$
1640 (s)	1635 (s)	1635 (s)	
1620 (s)	1600 (s)		v—C═C, v—C═N
1400 (m)	1490 (s)	1485 (m)	
1280 (w)	1260 (w)	1160 (w)	
1175 (m)	1170 (m)		δ—C—H
795 (m)	790 (s)	700 (s)	
950 (s)	950 (s)	940 (s)	
915 (s)	910 (s)	900 (s)	v—Mo—O
850 (s)	850 (s)	840 (s)	
730 (s)	715 (s)	700 (s)	
670 (s)	690 (s)	660 (s)	
620 (m)	620 (m)		δ—(O—Mo—O)
520 (s)	510 (s)	500 (m)	
405 (s)	405 (s)	390 (m)	
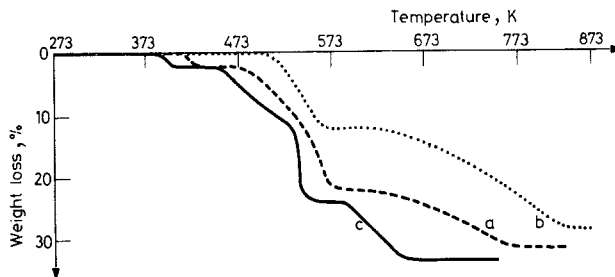
Fig. 1 Non-isothermal decomposition of 2,6-DMPO (a), 3,4-DMPO (b) and 2,4,6-TMPO (c)

correspond to the calculated weight loss of 2.18 and 2.11%, respectively, for the removal of two molecules of water from the parent compounds. The anhydrous materials are found to be stable up to 200° (2,6-DMPO), 230° (3,4-DMPO) and 165° (2,4,6-TMPO), and decomposition ceases at 540, 560 and 435°, respectively, giving molybdenum trioxide, identified by X-ray powder diffraction. The whole of the organic moiety was oxidized into gaseous products. The total decomposition in all cases is:

$$(\text{BH})_4\text{Mo}_8\text{O}_{26} \cdot n\text{H}_2\text{O(s)} \rightarrow 8\ \text{MoO}_3\text{(s)} + 4\ \text{B(g)} + 2\text{H}_2\text{O(g)} + n\text{H}_2\text{O(g)}$$

The anhydrous compounds decompose in two stages in the temperature ranges: 200–300° and 330–540° (2,5-DMPO), 230–290° and 310–560° (3,4-DMPO), and 165–263° and 330–435° (2,4,6-TMPO). The weight loss observed at the end of the first stage was found to be 22.18, 11.54 and 23.63%, respectively. Thus, it seems that only part of the gaseous decomposition products can leave the sample. This means that the decomposition proceeds by initial partial removal of the organic bases, followed by the evolution of a fraction of them to other compounds [16], with final subsequent combustion of the remaining products, besides transformation of the octamolybdate anion to MoO_3.

A comparison of the TG records of the studied compounds with those previously reported [5] (Table 3) shows the methylpyridine salts to be thermally more stable

Table 3 Initial and final decomposition temperatures of the first step

Compound	$T_i - T_f$, °C	Compound	$T_i - T_f$, °C
2,6-DMPO	200–300	2-MPO*	170–225
3,4-DMPO	230–290	3-MPO*	180–240
2,4,6-TMPO	165–263	4-MPO*	193–247
2,4-DMPO*	150–220	2-EPO*	137–214
2,5-DMPO*	187–265	3-EPO*	140–177
3,5-DMPO*	203–236	4-EPO*	150–220

* data from reference [5]

MP, EP, DMP: methyl-, ethyl- and dimethylpyridine respectively.

than ethylpyridine octamolybdates. On the other hand, the number of methyl groups has less influence on the stability than does the nature of the alkyl group. Finally, the position of the alkyl groups seems to be responsible for the thermal stability, which follows the sequence ortho < meta < para.

The kinetics of non-isothermal decomposition of 2,6-DMPO and 3,4-DMPO have been investigated in the first decomposition steps. The α vs. T plots (Fig. 2) are sigmoidal for both samples, with initial induction and acceleratory regions followed by a decay period. However, the induction region is practically non-existent for 3,4-DMPO, which contains no crystallization water.

Kinetic analysis of these steps was performed with the Satava integral method and the principal expressions of $g(\alpha)$ given in Table 4. The best fit of the experimental values corresponds to a random nucleation-controlled mechanism. The use of this method frequently requires a choice from among the six equally probable models (nucleation). It is possible to apply the data set to the Abou-Shaaban differential non-isothermal method, and in this way to obtain an independent estimation of the activation energy and frequency factor. The E_a value,
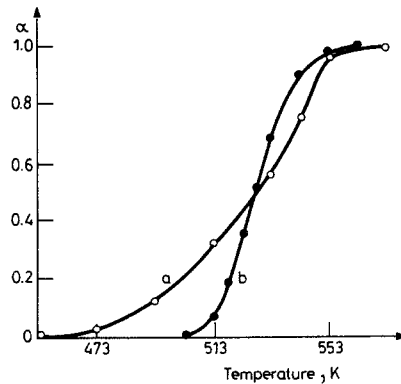
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Fig. 2 Fraction of material decomposed vs. temperature in the first step for 2,6-DMPO (a) and 3,4-DMPO (b)

Table 4 Kinetic models

1. Nucleation and		1.1 $n = 1/4$	
nucleus-growth		1.2 $n = 1/3$	
Kolmogorov, Erofeev,	$(-\ln(1-\alpha))^n$	1.3 $n = 1/2$	
Kazeev, Avrami and		1.4 $n = 2/3$	
Mampel (KEKAM)		1.5 $n = 1$	
		1.6 $n = 3/2$	
		2.1 $n = 1$	
2. Phase boundary	$1-(1-\alpha)^n$	2.2 $n = 1/2$	
		2.3 $n = 1/3$	
	α^2	3.1 one-dimensional	
3. Diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	3.2 two-dimensional	
	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	3.3 three-dimensional	
	$(1-(1-\alpha)^{1/3})^2$	3.4 three-dimensional	
		4.1 $n = 1/4$	
4. Potential law	$\alpha^n \ (0 < n < 2)$	4.2 $n = 1/3$	
		4.3 $n = 1/2$	
5. Reaction order	$1-(1-\alpha)^n$	5.1 $n = 2$	
		5.2 $n = 3$	

together with the correlation factor for the most probable equation model, corresponding to the Avrami–Erofeev equation with $n = 1$ (5.1 in Table 4), are 133.7 kJ/mol^{-1} ($r^2 = 0.9894$) and 120.9 kJ/mol^{-1} ($r^2 = 0.9926$) for 2,6-DMPO and 3,4-DMPO, respectively. This kinetic behaviour implies that the solids undergo decomposition by unimolecular decay.

Conclusions

Three new octamolybdates of organic bases derived from the pyridinium cation have been synthesized in order to study the solid-state decomposition of compounds more complex than those extensively studied (i.e. calcium carbonate, etc.) and to continue the comparative study with other similar octamolybdates.

The compounds were analyzed and characterized as β-octamolybdates by contrasting the spectroscopic data with the literature data [10–15] for octamolybdates whose structures have been obtained.

It is well known that thermal analysis curves can be used as fingerprints of the substances investigated within one laboratory only, as the measured data are very sensitive to the measuring circumstances, e.g. equipment, sample mass, heating rate etc. [17]. The thermal stability seems to follow the sequence 2,4,6-TMPO <2,6-DMPO <3,4-DMPO, if the minimum decomposition temperature, 165, 200 and 230°, respectively, is taken as a rough criterion of the stability. These results were compared with those previously reported [5]. The position and nature of the substituent in the pyridine ring have more influence than their number on the thermal stability of the octamolybdates.

Further, a kinetic study of the first decomposition step has been made for the two dimethyl compounds. A nucleation mechanism is proposed for the removal of the organic base in the two cases. The best fit corresponds to the equation $-\ln(1-\alpha) = kt$. Nevertheless, more experimental work (i.e. different heating rates, isothermal measurements, etc.) is required to confirm this fact. The E_a values obtained are very similar to those found for methylpyridinium octamolybdates [4] from isothermal studies and twice those obtained for the same compounds with the Satava method only [5]. Application of the Abou-Shaaban and Satava methods seems to be more adequate.

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Zusammenfassung — 2,6- und 3,4-Dimethylpyridinium- und 2,4,6-Trimethylpyridinium-octamolybdate wurden synthetisiert, charakterisiert und hinsichtlich ihrer thermischen Zersetzung untersucht. Die in der Reihenfolge 2,4,6-TMP <2,6-DMP <3,4-DMP zunehmende thermische Stabilität scheint mit der Stellung der Methylgruppen im Pyridinring in Zusammenhang zu stehen. Die kinetischen Parameter wurden für den ersten Zersetzungsschritt der zwei Dimethylpyridinium-octamolybdate berechnet. Ein Keimbildungsmechanismus wird vorgeschlagen. Die beste Näherung ergibt eine Gleichung, die auf einer zufälligen Keimbildung mit einem Keim pro Partikel basiert. Für die Aktivierungsenergie der 2,6- und 3,4-Derivate wurden Werte von 120,9 bzw. 133,7 kJ/mol^{-1} berechnet.

Резюме — Методом ТГ изучено термическое разложение синтезированных октамолибдатов 2,6- 3,4-диметил- и 2,4,6-триметилпиридиния. Термостойкость исследованных соединений располагается в ряд 2,4,6-триметилпиридиний <2,6-диметилпиридиний <3,4-диметилпиридиний и связана с расположением метильных групп в пиридиновом кольце. Определены кинетические параметры первой стадии разложения двух октамолибдатов диметилпиридиния. Реакция разложения лучше всего согласуется с механизмом произвольного образования центров кристаллизации: на одну частицу приходится один центр кристаллизации. Энергии активации, вычисленные для 2,6- и 3,4-производных, составляли, соответственно, 120,9 и 133,7 кдж·моль$^{-1}$.