Thermochimica Acta, 21 (1977) 135–141
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THERMOGRAVIMETRIC INVESTIGATIONS IN DYNAMICAL REGIME ON SOME TETRAMOLYBDATES OF ORGANIC BASES

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(Received 8 December 1976)

ABSTRACT

A systematic study about the thermal decomposition kinetics in function of the substituted bases in $(BH)_2Mo_4O_{13}$ type compounds shows a decomposition pattern with three or two steps which are controlled by a random nucleation mechanism.

The thermal stability as well as the activation energy is studied as a function of the nature of the base, its symmetry and its pK_a.

INTRODUCTION

We have recently investigated the thermal decomposition kinetics of some molybdates of organic bases of general formula $(BH)_2Mo_4O_{13}$ with B = pyridine (BP), 2-methyl pyridine (M2), 3-methyl pyridine (M3), 4-methyl pyridine (M4) and quinoline (BQ)[1-3]. Only a few studies on the thermal decomposition of pyridine molybdates have been made in the past[1-4].

In this paper the thermal decomposition kinetics of some new tetramolybdates of organic bases is studied by thermogravimetry and differential scanning calorimetry. The bases were 2-, 3- and 4-ethylpyridine (E2, E3 and E4); 2,4-; 2,5- and 3,5-dimethylpyridine (L1, L2 and L3) and 2-, 3- and 4-aminopyridine (A2, A3 and A4). This study lies within the scope of our program of systematic investigation on molybdates of organic bases in two aspects: solid phase and dissolution.

For comparison with previous studies[1-3] the kinetic study was made in a dynamic regime and the theoretical analysis by means of the Šatavá method. Therefore, all the symbols used here are the same as in refs. 1, 3 and 5.

EXPERIMENTAL

The compounds were prepared for the first time in our laboratory and the experimental process, X-ray and infrared characterizations as well as the study in dissolution are described in refs. 6 and 7.

All the compounds have a low solubility in water and in the usual organic solvents. In the case of the ethyl-compounds small crystals were obtained by means of a slow evaporation. From infrared studies it seems that there is no coordination bonding between the base and the metal. Moreover, the base seems protonated.

The apparatus as well as the experimental conditions were described in refs. 8 and 9. Three runs were made on all the samples with a very good reproducibility. The spread in the processed data is shown on each figure of the paper.

RESULTS AND DISCUSSION

From thermogravimetric and calorimetric curves we can obtain the stability interval for each compound studied (Table 1). The experimental results indicate that the pathway is not as simple as that found for the methyl compounds[1]. Most of the decomposition curves for all the compounds studied exhibit a decomposition pattern with three steps (exceptions are shown in Table 1) leading to a residual weight equal to that expected for MoO_3. This point was confirmed by means of X-ray diffraction.

It is obvious from this investigation that the decomposition is a function of the nature of the base, its symmetry and its pK_a. The weight loss for each step only reveals a clear pattern in the following cases:

(a) For the E3 and E4 compounds:

1st step: $(BH)_2Mo_4O_{13} \rightarrow 4Mo\ O_3\frac{3}{2}B + \frac{1}{2}B + H_2O$
2nd step: $4Mo\ O_3\frac{3}{2}B \rightarrow 4Mo\ O_3\frac{1}{2}B + B$
3nd step: $4Mo\ O_3\frac{1}{2}B \rightarrow 4MoO_3 + \frac{1}{2}B$

(b) For the E2 and L3 compounds:

1st step: $(BH)_2Mo_4O_{13} \rightarrow 4MoO_3B + B + H_2O$
2nd step: $4MoO_3 \rightarrow 4MoO_3\ \frac{1}{2}B + \frac{1}{2}B$
3nd step: $4Mo\ O_3\frac{1}{2}B \rightarrow 4MoO_3 + \frac{1}{2}B$

From a very careful analysis of the TG curves in the case of 2-methylpyridine (M2)[1] one can conclude that this compound also shows a three step decomposition pattern which is similar to that for the E2-compound. This is not the case for the 3- and 4-methyl pyridine for which the pattern shown in ref. 1 seems valid. The special behaviour for the A2, M2 and E2 compounds in every family can be explained with the pk_a of the base (see Fig. 5).

The patterns derived from the TG curves for the other compounds are not shown here because we think that another kind of identification is required. However, the experimental results permit us to write the global process as follows:

$$(BH)_2\ Mo_4O_{13} \rightarrow 4MoO_3 + 2B + H_2O$$

Special attention must be paid in this case to the shape of the α vs. T curves. Figures 1 and 2 show four typical curves selected among all the compounds studied.

TABLE 1

ACTIVATION ENERGY, INITIAL TEMPERATURE AND FINAL TEMPERATURE OF DECOMPOSITION AND WEIGHT LOSS FOR EACH DECOMPOSITION STEP OF THE COMPOUNDS STUDIED

Compound	*No.*[a]	*1st step*				*2nd step*				*3rd step*			
		$T_i(K)$	$T_f(K)$	%[b]	$E_a(kJ\ mol^{-1})$	T_i	T_f	%	E_a	T_i	T_f	%	E_a
BP[c]	1	484	527	18.65	83	527	603	23.57	34	—	—	—	—
M2[c]	2	443	498	14.56	50	498	573	19.86	29	573	693	25.82	30
M3[c]	3	453	513	18.00	52	513	633	25.90	18	—	—	—	—
M4[c]	4	466	520	10.55	53	562	743	25.44	31	—	—	—	—
E2	5	308	487	13.53	25	487	709	21.96	13	709	813	29.33	50
E3	6	413	450	8.97	45	450	553	21.68	23	661	704	28.59	82
E4	7	423	493	8.84	39	493	733	22.50	16	733	783	28.88	46
L1	8	431	524	21.07	45	643	753	28.45	36	—	—	—	42
L2	9	460	538	18.69	27	603	743	28.12	39	—	—	—	—
L3	10	476	509	16.00	64	509	571	22.10	25	571	685	28.88	33
A2	11	495	546	14.34	35	577	623	20.36	37	623	704	26.38	16
A3	12	504	562	8.32	22	562	628	16.65	15	628	691	26.38	26
A4	13	531	591	11.33	32	599	658	23.37	35	658	691	26.36	52

[a] This number is used in Figs. 3, 4, 5 and 6. [b] %, shows the weight loss from the beginning to every step. [c] From ref. 3, with the modification shown in the text about M2.

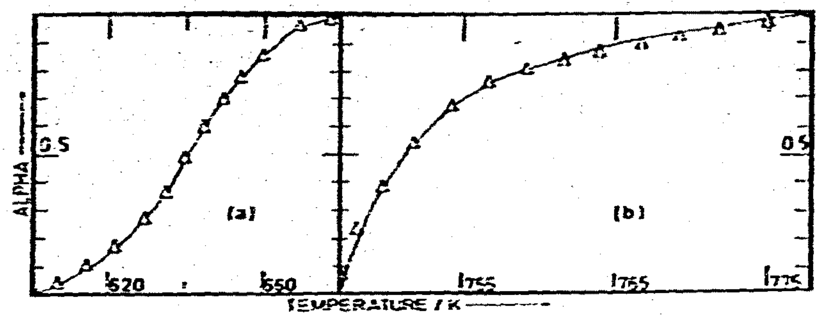

Fig. 1. Fraction of decomposed material (α) vs. temperature for the second step of A4 (a) and the third step of E4 (b).

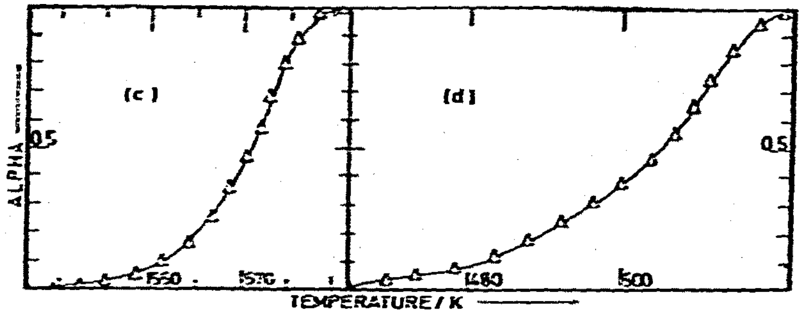

Fig. 2. Fraction of decomposed material (α) vs. temperature for the first step of A4 (c) and the second step of L1 (d).

Figure 2c shows the first step for the A4 compound. The shape of this curve shows a reaction with an initial acceleratory period followed by a deceleratory one in which the reaction rate is lower. In Fig. 1a, which shows the second step of the A4 compound, we can see that the initial acceleratory period is considerably reduced and in Fig. 1b for the third step of the E4 compound this initial acceleratory period practically disappears. Figure 2d shows the second step for the L1 compound which presents a more complex behaviour than in the other cases. In the first part we have an initial slow reaction during which the decomposition begins until a value of $\alpha \simeq 0.1$ is reached. In the second part with $0.1 < \alpha < 1$, the behaviour is similar to that which appears in Fig. 1a or 2c. The α vs. T curves for each step of all compounds studied are similar to those shown in Figs. 1 and 2.

From Figs. 3 and 4 we can see that the straight line criterion is fulfilled in the three steps of all the compounds by an equation with a random nucleation as rate-determining process within the accuracy of Šatavá's method [3].The rate-determining process must be related with the structure of the compound[8], and in our case we can make some considerations on this point although the structure of the compounds is unknown. The organic part must produce a decrease in the free energy which gives good conditions for the appearance of "activated fluctuations" in the sample which can produce a larger number of nuclei with the critical size required to begin the decomposition following a random nucleation mechanism. One observes that the

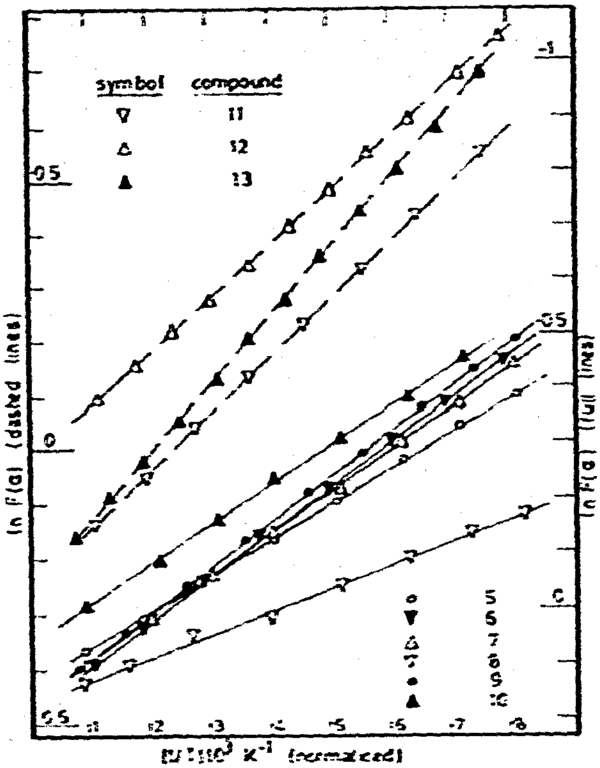

Fig. 3. Validity of the random nucleation mechanism function ln [− ln (1 − α)]$^{1/3}$ vs. 1/T for the first step of all the compounds studied. The abscissa scale for each compound appears in Table 2.

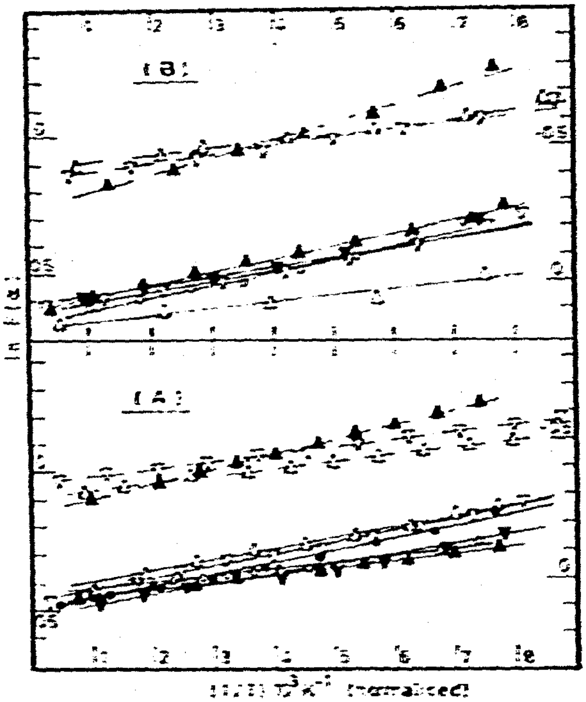

Fig. 4. Validity of the random nucleation mechanism function ln [− ln (1 − α)]$^{1/3}$ vs. 1/T for the second (a) and the third (b) steps of all the compounds studied. All the symbols are the same as those which appear in Fig. 3 and the abscissa scale is explained in Table 2.

TABLE 2

EXPLANATION FOR THE ABSCISES AXIS FOR THE FIGS. 3, 4A AND 4B

Compound	*1st step*		*2nd step*		*3rd step*	
	a[a]	b[b]	a	b	a	b
E2	2.09	0.04	1.40	0.10	1.275	0.02
E3	2.22	0.02	1.875	0.05	1.435	0.01
E4	2.05	0.025	1.35	0.10	1.297	0.005
L1	2.16	0.12/9	1.945	0.02	1.38	0.02
L2	1.91	0.02	1.413	0.025	—	—
L3	1.98	0.12/9	1.78	0.025	1.555	0.03
A2	1.85	0.02	1.62	0.04/3	1.44	0.02
A3	1.79	0.08/3	1.61	0.02	1.456	0.08/5
A4	1.71	0.08/3	1.53	0.02	1.45	0.01

[a] The value for the first division (1) in the abscissa axis. [b] Interval between each division.

deviations from the straight line increase from the 1st to the 3rd step. This shows that the process becomes more complex as it goes on with our experimental conditions.

The activation energy values as well as the initial and final temperatures for each step are shown in Table I. Figure 5 shows the relationship between the pK_a

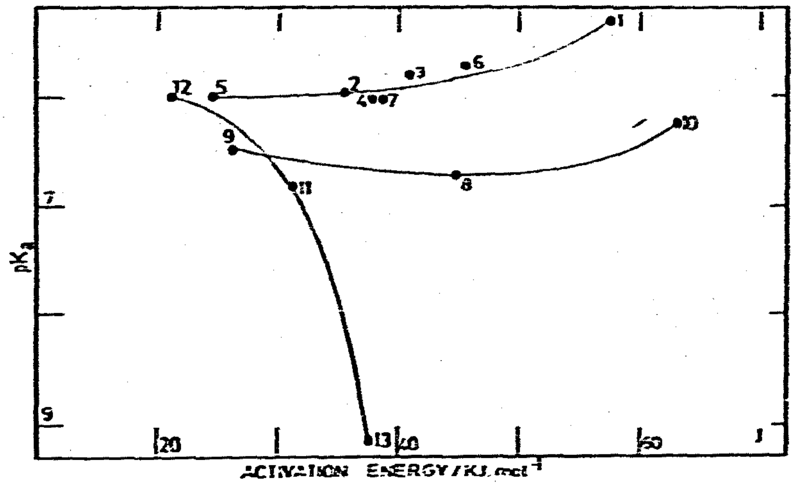

Fig. 5. pK_a of the bases vs. activation energy for the first step of the decomposition. The equivalent compound number is shown in Table I.

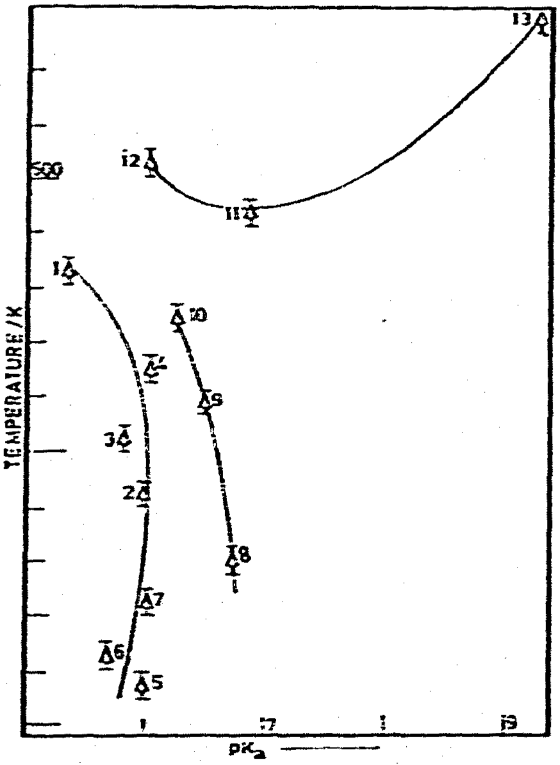

Fig. 6. Initial decomposition temperature vs. pK_a of the organic bases. The equivalent compound number is the same as that in Fig. 5.

values of the organic bases and the activation energies for the first step of the decomposition. The same representation is shown in Fig. 6 for the initial temperature of decomposition. In both figures the curves are drawn for the sake of comprehension. From these figures, it is not possible to find a simple relation between the parameters E_a–pK_a and T–pK_a for all the compounds studied but some comments are possible.

Compounds with the methyl or ethyl groups show a different behaviour from those with NH_2 group. While the A compounds present a clear correlation between the pK_a of the organic bases and the order of the experimental values for the activation energies, this is not the case for the methyl and ethyl compounds, although these results are in disagreement with those found by means of isothermal runs[3].

From Fig. 6 similar considerations can be made, but in this case only the L-compounds seem to show a correlation between the pK_a and the initial temperatures of decomposition. Moreover, this parameter seems to have a closer connection with the symmetry and steric effects. In this sense the following relations are obtained: $T_2 < T_3 < T_4 < T_1$; $T_5 < T_6 < T_7$; $T_8 < T_9 < T_{10}$; and $T_{11} < T_{12} < T_{13}$. We can also study the influence on the stability of the nature of the group incorporated to the ring: The order of stability is for A compounds > for M compounds > for E compounds. The L compounds show an order of stability similar to that of the M compounds.

For the other step, it is not possible to make similar comments because the properties of the compounds, which are formed in every step of the decomposition, are unknown. The decomposition study of these compounds by means of isothermal techniques is being continued at present in our laboratory.

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