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THERMAL DECOMPOSITION KINETICS OF SOME MOLYBDATES OF ORGANIC BASES

M. J. TELLO
Facultad de Ciencias, Dto. de Física, Granada (Spain)
E. H. BOCANEGRA
Facultad de Ciencias, Dto. de Física, Apdo. 644, Bilbao (Spain)
P. GILI, L. LORENTE AND P. ROMAN
Facultad de Ciencias, Dto. de Química, Apdo. 644, Bilbao (Spain)
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ABSTRACT

$(BH)_2Mo_4O_{13}$ compounds (B = pyridine, 2-methyl pyridine, 3-methyl pyridine, 4-methyl pyridine and quinoline) present experimental decomposition curves with two steps which are controlled by a random nucleation mechanism.

The activation energy values found were between 4 and 6 kcal mol^{-1} for the first step and between 2 and 3 kcal mol^{-1} for the second step.

INTRODUCTION

Some molybdates of organic bases (ethylamine, tetramethylamine, phenylamine and pyridine) were synthetised by Sonnenscheim[1], Classen[2], Ditte[3] and Pincusshon[4]. Krause and Krauskopf[5] made one more complete description of these compounds. More recently Camelot[6] has reported an infrared study on the addition compounds of pyridine with oxides of chromium, molybdenum and uranium where the oxidation state of the metal is VI.

Only a few studies on the thermal decomposition of pyridine molybdates have been made by Schwing-Weill[7–9] but no systematic works in the literature seem to have reported about this problem.

In this paper we present an initial study on decomposition kinetics in the dynamical regime of the $(BH)_2Mo_4O_{13}$ compounds (B = pyridine-BP, 2-methyl pyridine-B2, 3-methyl pyridine-B3, 4-methyl pyridine-B4 and quinoline-BQ). These compounds (except BP) were synthetised for the first time in our laboratory[10] as part of our programme of investigation on molybdates of organic bases.

The kinetic study will be based on the Šatava method and therefore all the symbols used here are the same as in ref. 11.

EXPERIMENTAL

The compounds were prepared as noted previously[10] but in this case the experimental process was carried out twice and the purity of the compounds was better than in ref. 10. Also it should be noted that with a slow evaporation very small crystals were obtained. All the compounds have a low solubility in water and they are insoluble in the usual organic solvents.

Table 1 shows the results of the chemical analysis. The X-ray and infrared characterizations were described in ref. 10.

TABLE 1

RESULTS OF THE CHEMICAL ANALYSIS OF SOME MOLYBDATES

Compound	MoO_3		*C*		*H*		*N*	
	Exp.	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*
BP	76.52	76.59	16.01	15.98	1.63	1.61	3.77	3.73
B2	73.96	73.84	18.38	18.48	2.08	2.07	3.65	3.59
B3	73.68	73.84	18.38	18.48	2.12	2.07	3.52	3.59
B4	73.67	73.84	18.37	18.48	2.14	2.07	3.60	3.59
BQ	67.62	67.57	25.41	25.37	1.92	1.89	3.19	3.29

The instrument used for the thermal measurements was a Perkin-Elmer thermobalance and the experimental conditions were already explained in ref. 12. The initial temperature of decomposition was confirmed by using a Perkin-Elmer DSC calorimeter with a very good calibration by using ferroelectric standards[13].

RESULTS AND DISCUSSION

The decomposition curves exhibited a small overlap of both decomposition steps for BP and BQ and, for the other compounds examined, a stability interval for the compounds formed during the first decomposition step. The overlap concerns only a small part of the curves and both the initial and the final weight can be defined. Consequently, values of E_a may be calculated. The weight loss during both steps for B2, B3 and B4 support the following pattern:

1st step: $4MoO_3\cdot 2C_6H_7N\cdot H_2O \rightarrow 4MoO_3\cdot C_6H_7N+C_6H_7N+H_2O$

2nd step: $4MoO_3\cdot C_6H_7N \rightarrow 4MoO_3+C_6H_7N$

but a further characterization is necessary.

The decomposition curve for BP presented a similarity with the decomposition curve of the compound formed during the first decomposition steps of both $3MoO_3\cdot 2C_5H_5N\cdot H_2O$ and $4MoO_3\cdot 3C_5H_5N\cdot H_2O$ in ref. 8. It should also be noted that the temperature interval of decomposition is the same as that of the compound formed during the first step in curve Ic in ref. 8. A coherent decomposition pattern for both BP and BQ cannot be given now.

TABLE 2

E_a, T_i AND T_f FOR THE TWO DECOMPOSITION STEPS FOR THE COMPOUNDS STUDIED

Compound	*1 st step*			*2nd step*		
	T_i (*K*)	T_f (*K*)	E_a (*kcal mol*$^{-1}$)	T_i (*K*)	T_f (*K*)	E_a (*kcal mol*$^{-1}$)
BP	484	527	6.12	527	587	2.69
B2	442	500	3.75	505	554	2.33
B3	453	508	4.61	525	587	2.19
B4	458	525	4.85	563	635	2.11
BQ	471	531	5.36	531	611	2.13

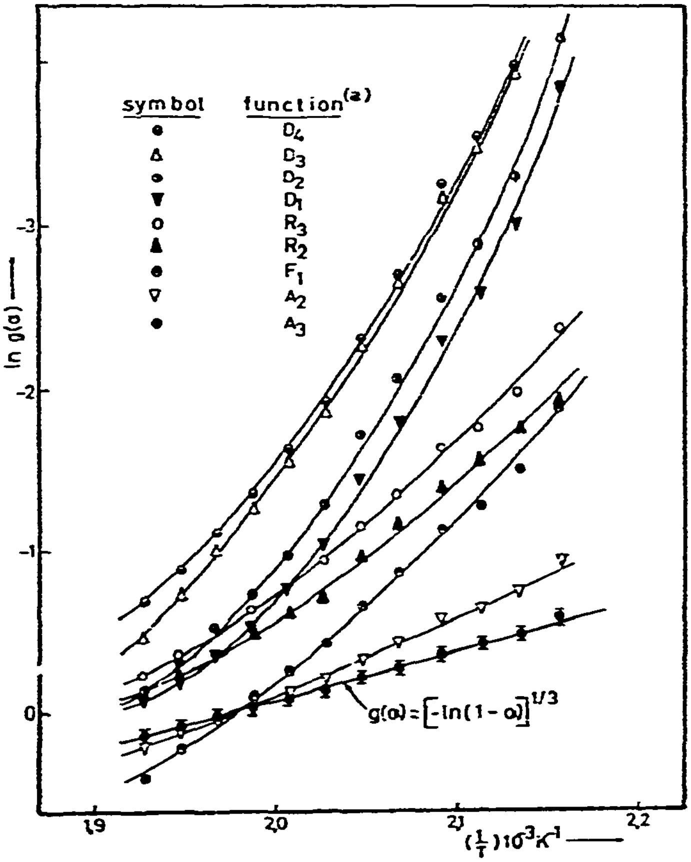

Fig. 1. Šatava's representations for the first step in B4-compounds. (a) See ref. 11.

Table 2 shows the initial and final temperature for the two decomposition steps for each compound studied. No exact correlation exists between the pK_a of the organic bases and the order of the experimental values for the initial temperatures of decomposition. Moreover, this experimental order seems reasonable if the symmetry and steric effects are taken into account, with the exception of the relation BP–BQ and there is no obvious reason now to explain this "irregular" behavior.

Figures 1 and 2 show the plotting of the Šatava's analysis for both decomposition steps. Similar plottings were observed for all other compounds examined. We can see that the straight line criterium shows that both decomposition steps are controlled by a random nucleation mechanism.

The temperature interval for each decomposition step permits a simplified treatment for the estimation of the activation energy[11] and the values found are shown in Table 2.

The activation energy values for the first step show the same relation as the initial decomposition temperatures while for the second step the values found present a similarity in the experimental error which seems to confirm the decomposition

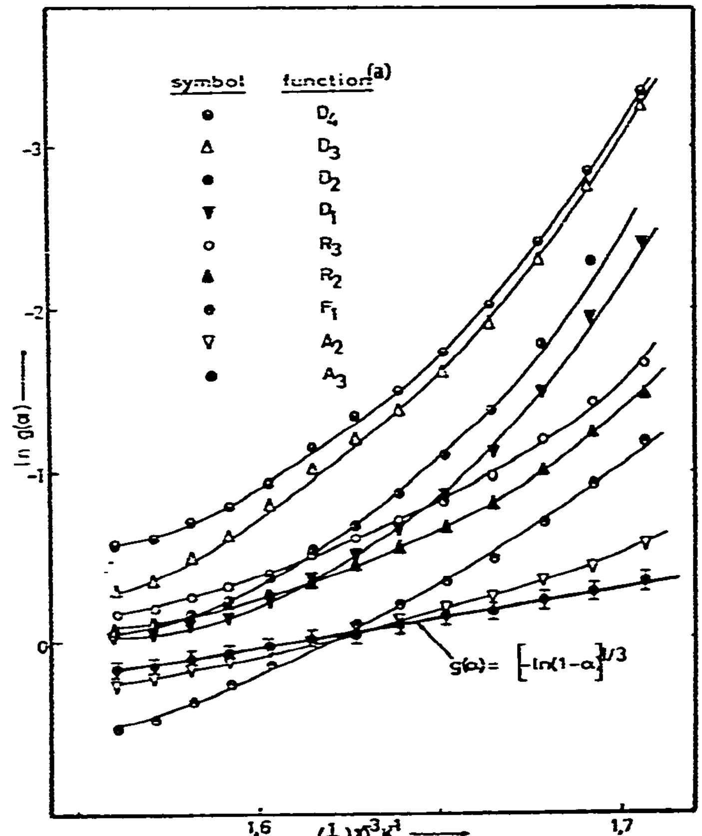

Fig. 2. Šatava's representation for the second step in B4-compounds. (a) See ref. 11.

pattern about the formation of the addition compounds in the first step of the decomposition.

A study about the chemical properties as well as kinetic parameters is in preparation.

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