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THERMAL DECOMPOSITION OF $(C_6H_5\text{–}NH_3)_4Mo_8O_{26} \cdot 2H_2O$. ISOTHERMAL AND NON-ISOTHERMAL KINETIC ANALYSIS

C. SANTIAGO and A.R. ARNAIZ

Departamento de Química (Inorgânica), Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, Bilbao (Spain)

A. IRABIEN

Departamento de Química Tecnica, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, Bilbao (Spain)

M. MARTINEZ

Departamento de Química, Facultad de Química, Universidad Compultense, Madrid (Spain)

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ABSTRACT

The thermal decomposition of anilinium octamolybdate dihydrate, in powder form, has been studied by thermogravimetry (TG) under isothermal and non-isothermal experimental conditions.

The TG curve shows that, after dehydration, decomposition of the compound starts at 473 K. This first decomposition step has also been studied in isothermal runs, between 448 and 493 K.

Although a complex reaction takes place, the kinetic model could be the same in both regimes: phase boundary reaction with spherical symmetry. However, the data at high temperatures under an isothermal regime are better fitted to a diffusion with cylindrical symmetry reaction model, probably due to the symmetry of the crucible.

Activation energy an frequency factor values have been calculated in both cases. Explanations for the differences are also given.

INTRODUCTION

The thermal decomposition of polymetalates has been studied by several authors [1–8] in recent years by means of thermoanalytical methods. In some cases, supplementary methods [9–11] are used to find intermediate phases in order to describe the chemical reactions taking place along with the process. However, most of these investigations are based on the suppositions that the initial compounds have different numbers of simple decomposition steps, and that each reaction takes place at a different temperature. This means that the weight loss is explained through stoichiometric amounts of water, ammonia or organic bases coming from the initial solid.

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The influence of experimental conditions and the difference between using isothermal or non-isothermal conditions in gas–solid kinetic studies have been the subject of many studies [12–14].

Assuming a simple reaction scheme, some pyridinium polymolybdates have previously been studied under nonisothermal and isothermal regimes [15].

The TG curve for anilinium octamolybdate dihydrate shows three decomposition steps, dehydration being the first reaction, as has been explained [16]. The second step corresponds to the decomposition of anilinium. Different organic compounds have been identified in the solid residues left at the end of this step, in both dynamic and isothermal runs, and they are different for both regimes [17,18]. In the last decomposition step, these organic compounds are lost from the system leading to a residual weight corresponding to molybdenum trioxide, which has been identified from X-ray diffraction patterns.

In the present work a new step is made in understanding the thermochemical behavior of this compound by a comparative study between the kinetic parameters obtained under isothermal and non-isothermal regimes, for the first decomposition step. Although a complex reaction scheme takes place which depends on the experimental conditions, the resultant kinetic model is nearly the same in both dynamic and isothermal regimes.

The influence of the complex reaction scheme could be applied to the activation energy and frequency factor values.

EXPERIMENTAL

The experimental technique, calibrations, conditions, sample preparation, and synthesis and characterization of the anylinium octamolybdate dihydrate were described in a previous work [16].

RESULTS AND DISCUSSION

The thermal decomposition of the compound starts at 473 K after dehydration has taken place, and seems to have two different decomposition steps in the non-isothermal thermogravimetric runs: first step, 473–511 K; second step, 573–743 K.

The weight loss at the end of the first step (4.90%) cannot be explained with a simple reaction scheme. Besides, a series of intermediate organic compounds, which are different from aniline, has been identified in black solid samples obtained on stopping the decomposition at 568 K [17,18].

The first decomposition step was also studied by means of thermogravimetric decomposition under an isothermal regime in the range 448–493 K. Results are given in Table 1.

TABLE 1

Isothermal decomposition between 448 and 493 K: weight loss percentage and time for each curve

T (K)	448	458	468	473	483	488	493
Weight loss (%)	1.45	2.25	4.60	5.40	6.60	6.50	6.70
t (min)	154	93	65	68	65	36	20

The organic products in the solid samples from isothermal decomposition at 568 K (weight loss 14%) are different from those in samples from non-isothermal runs, as shown in Fig. 1. Peaks (1) and (2) in chromatogram

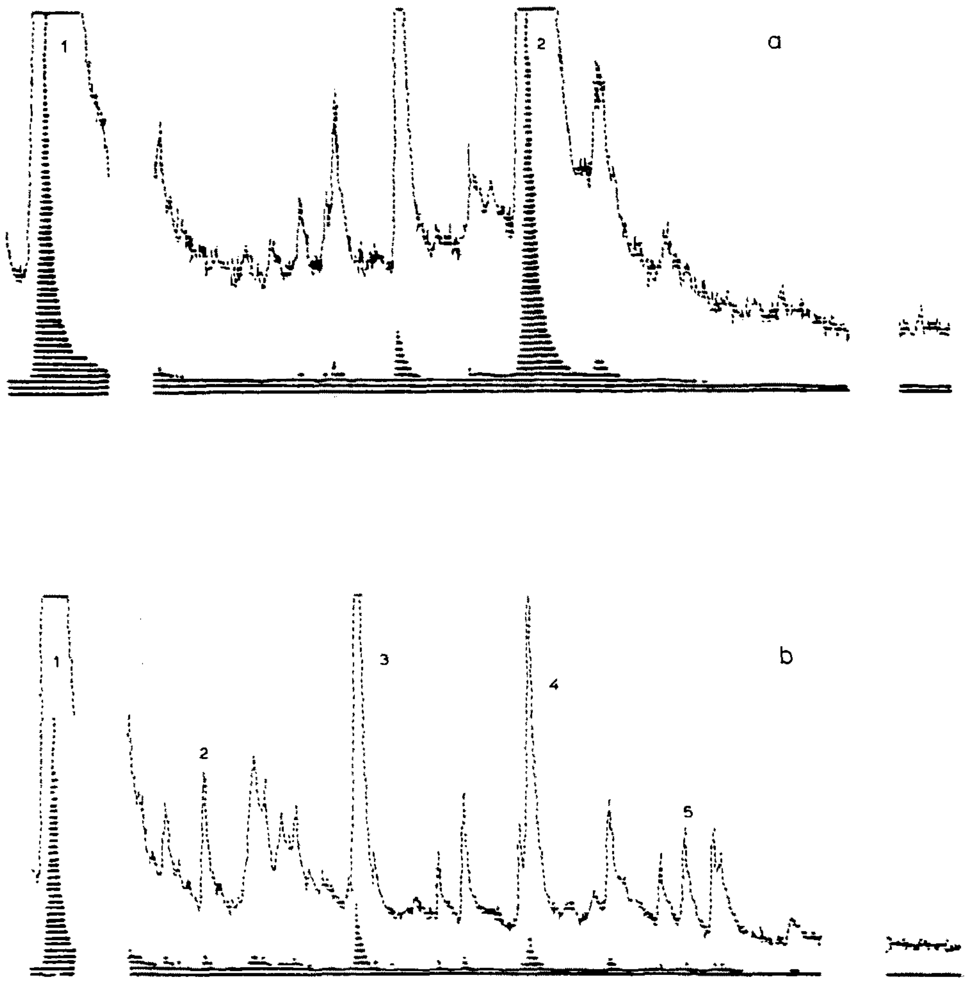

Fig. 1. Chromatograms obtained by the GC/MS technique: (a) sample from non-isothermal decomposition; (b) sample from isothermal decomposition.

TABLE 2

Scheme of treatment of isothermal data for the different models

Kinetic model	Y-axis	X-axis	Origin ordinate	Slope
KEKAM = *1*	$\ln[-\ln(1-\alpha)]$	$\ln t$	$\ln K$	$N=1/n$
Phase boundary reaction				
plane symm. = 2.1	$1-(1-\alpha)=\alpha$	t	0	K
cylind. symm. = 2.2	$1-(1-\alpha)^{1/2}$	t	0	K
spherical symm. = 2.3	$1-(1-\alpha)^{1/3}$	t	0	K
Diffusion				
plane symm. = 3.1	α^2	t	0	K
cylind. symm. = 3.2	$(1-\alpha)\ln(1-\alpha)+\alpha$	t	0	K
spherical symm. = 3.3	$1-3(1-\alpha)^{2/3}+2(1-\alpha)$	t	0	K
Potential law = *4*	$\ln t$	$\ln \alpha$	$-\ln K$	n
Reaction order				
order 2 = 5.1	t	$1-(1-\alpha)^2$	0	$1/K$
order 3 = 5.2	t	$1-(1-\alpha)^3$	0	$1/K$

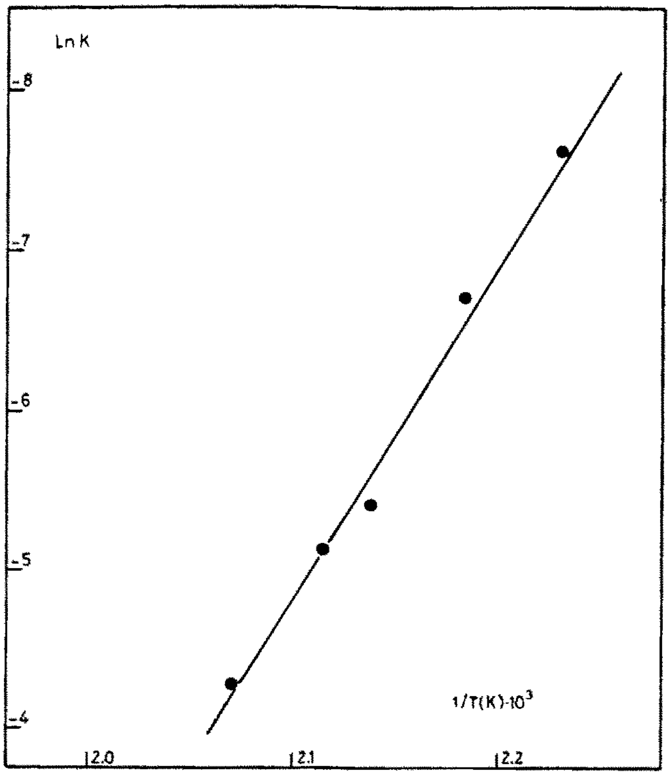

Fig. 2. Arrhenius plot of the kinetic parameters from the phase boundary reaction with spherical symmetry.

TABLE 3

Least-squares fit for the scheme in Table 2

T (K)	Model 1			Model 2.1		Model 2.2		Model 2.3		Model 3.1	
	N	ln K	r^2	K	r^2	K	r^2	K	r^2	K	r^2
448	0.93	−6.017	0.937	0.00136	0.962	0.00072	0.968	0.00049	0.998	0.00031	0.966
458	0.56	−3.525	0.974	0.00315	0.945	0.00177	0.958	0.00122	0.992	0.00124	0.974
468	0.65	−2.741	0.970	0.00929	0.964	0.00610	0.988	0.00447	0.992	0.00727	0.978
473	0.75	−2.912	0.964	0.01101	0.955	0.00777	0.994	0.00586	0.986	0.00984	0.978
483	0.67	−1.712	0.941	0.02052	0.881	0.01715	0.980	0.01380	0.993	0.02321	0.990
488	0.74	−1.646	0.970	0.02672	0.780	0.02253	0.924	0.01818	0.956	0.03064	0.956
493	1.00	−1.232	0.883	0.04542	0.550	0.04728	0.863	0.04466	0.956	0.05390	0.769

T (K)	Model 3.2		Model 3.3		Model 4			Model 5.1		Model 5.2	
	K	r^2	K	r^2	n	− ln K	r^2	K	r^2	K	r^2
448	0.00016	0.96	0.00004	0.958	1.12	6.64	0.929	0.00242	0.949	0.00323	0.931
458	0.00070	0.97	0.00016	0.966	1.92	6.73	0.984	0.00507	0.910	0.00615	0.870
468	0.00491	0.947	0.00122	0.933	1.85	4.97	0.994	0.01131	0.865	0.01095	0.734
473	0.00721	0.939	0.00186	0.918	1.64	4.61	0.992	0.01219	0.671	0.01124	0.616
483	0.01960	0.988	0.00543	0.970	2.17	3.76	0.996	0.01784	0.640	0.01402	0.449
448	0.02603	0.990	0.00722	0.991	1.92	3.25	0.904	0.02280	0.464	0.01769	0.262
493	0.05372	0.992	0.01720	0.986	1.56	2.41	0.706	0.03693	0.270	0.03089	0.168

(a) have been identified as indole and benzylazo-(2-phenyl)-ethane, respectively, while peaks (1)–(5) in chromatogram (b) are found to be *N*-ethylaniline; *N*,*N*-diethylaniline; *N*-pyridylaniline; *N*-alkyl or *N*,*N*-dialkylaniline; and benzylazo-(2-phenyl)-ethane, respectively. From these results a very complex reaction scheme must be assumed in order to explain the different weight losses in the reaction, as has been shown in refs. 17 and 18.

The isothermal data were treated by linear regression for the models shown in Table 2.

A least-squares fit for the different models is shown in Table 3. In this table, it can be seen that the best fitting is obtained for a phase boundary reaction with decreasing spherical symmetry. However, at highest temperature the best fitting is obtained for a model of diffusion with cylindrical symmetry. This could be due to the experimental conditions, for instance the symmetry of the crucible.

From the Arrhenius plot the activation energy ($E = 178.10$ kJ mol^{-1}) and pre-exponential factor ($A = 1.49 \times 10^{19}$ min^{-1}) have been obtained as shown in Fig. 2. The correlation coefficient for the least-squares fit is $r^2 = 0.991$.

Non-isothermal α–T data were also used to obtain kinetic parameters by means of Šatava's analysis [19] and Abou-Shaaban's method [20], for the same kinetic models as used before. Results are given in Table 4 for each model along with the correlation coefficient for the least-squares fit.

It is not easy to discriminate the kinetic model between phase boundary

TABLE 4

Kinetic parameters and correlation coefficients from non-isothermal data for the kinetic models in Table 2

Model	N	E (kJ mol^{-1})	A (min^{-1})	r^2
1	2/3	277	3.32×10^{19}	0.927
	1	182	2.49×10^{18}	0.927
	3/2	118	4.19×10^{16}	0.927
	2	86.5	5.92×10^{14}	0.927
	3	54.8	7.98×10^{10}	0.927
	4	38.9	7.32×10^{6}	0.927
2.1		138	4.15×10^{13}	0.984
2.2		157	2.74×10^{15}	0.972
2.3		165	1.21×10^{16}	0.962
3.1		285	7.74×10^{28}	0.984
3.2		308	1.28×10^{31}	0.980
3.3		318	3.39×10^{4}	0.974
	n			
4	1/2	64.8	6.66×10^{5}	0.984
	1/3	40.3	1.39×10^{3}	0.984
	1/4	28.1	5.63×10^{1}	0.984
5.1	2	111	7.08×10^{10}	0.958
5.2	3	92.4	8.46×10^{8}	0.895
Abou-Shaaban		161	3.50×10^{16}	0.976

reaction, diffusion and potential laws because of the similar values of r^2, none of which are very good.

The E and A values for phase boundary reaction with spherical symmetry (165.0 kJ mol^{-1} and 1.21×10^{16} min^{-1}, respectively) can be compared with those obtained from isothermal data.

The activation energy values are similar, which could indicate similar chemical reactions. However, different values of the pre-exponential factors could mean changes in the kinetic reactions. This problem can be explained taking into account different catalytic reactions on the molybdate anion or molybdenum trioxide, leading to different organic products, as has been shown earlier [17,18].

CONCLUSIONS

The first decomposition step of anilinium octamolybdate by means of thermogravimetric analysis has been studied under dynamic and isothermal regimes. The change in the complex chemical reaction scheme with temperature has indicated the difficulty of discriminating the kinetic model from dynamic methods.

Models developed to describe solid decomposition reactions usually allow the simplification of assuming that the kinetic behavior is the same during the whole transformation. However, it is possible to have a change in the reaction mechanism or controlling step during a decomposition run [21]. Besides, the major influence of the temperature change can mask the minor influence of the conversion change in the decomposition rate [22,23]. Therefore, the isothermal method seems more suitable in this case for the elucidation of the most probable kinetic model and parameters.

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