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Note

Influence of isothermal and dynamic runs on the kinetic parameters of thermal decompositions

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The influence of the experimental conditions as well as the difference between the use of dynamical or isothermal regimes in solid state kinetic studies employing thermogravimetric techniques has a considerable interest[1-4]. If we take into account that the data related with the decomposition of not previously investigated compounds are most interesting in order to identify a substance and to determine the amount of it present in a sample, any effort to achieve the experimental conditions for universal reproductibility is an interesting scope within this complicated problem.

In this paper a new step is given in this way by a comparative study between the kinetic parameters obtained by means of both dynamical and isothermal regimes. The compounds used in this study were some molybdates of organic bases $(BH)_2Mo_4O_{13}$ (B = pyridine-BP, 2 methyl pyridine-B2, 3 methyl pyridine-B3 and 4 methyl pyridine-B4) which were the subject of previous studies[5,6] in our laboratory. These compounds present a more complicated behaviour than those referred to in other publications which deal with the same type of problems[2-4].

EXPERIMENTAL

The experimental technique, calibration as well as the sample preparation were described in previous communications[1,5,7]. Special attention was paid to the experimental conditions in this case. For the dynamical regime new runs were made in which the sample was heated to 10 °C below the reaction temperature and it was then allowed to stay for 1/2 h at this temperature with a dry nitrogen flow of 50 ml min^{-1}. When the homogenization conditions were accomplished the run was started at a heating rate of 5 °C min^{-1} and a dry nitrogen flux of 25 ml min^{-1}.

In the isothermal case the sample was also pre-heated near the reaction temperature in order to avoid the artificial induction and acceleratory periods.

The run is then initiated with a dry nitrogen flux of 25 ml min^{-1} and the temperature at which the run starts is reached with a high heating rate of 360 K min^{-1} during some seconds.

The nature of the samples was fine powder with a mass between 10 and 15 mg for comparison with previous results[5].

RESULTS AND DISCUSSION

The compounds studied present a two-step decomposition pattern[5] with the formation of addition compounds in the intermediate step and MoO_3 as final decomposition product. The mass loss for each of the several samples was determined as a time function in the isothermal regime. The values of α were plotted for comparison following the nine equations given in ref. 5. Appropriate equations were determined by visual inspection of their linearity and least squares fit. In this case the three random nucleation equations (F_1, A_2 and A_3 in refs. 5 and 8) present very near correlation factors which involve an unlike behaviour from the experimental results obtained from the dynamical regime. The choice of equation A_3 was then based on the clearer plot from the dynamical regime. Typical rate plots are shown in Fig. 1 for the first decomposition step for the B4 compound. Similar plottings were observed for all other compounds studied.

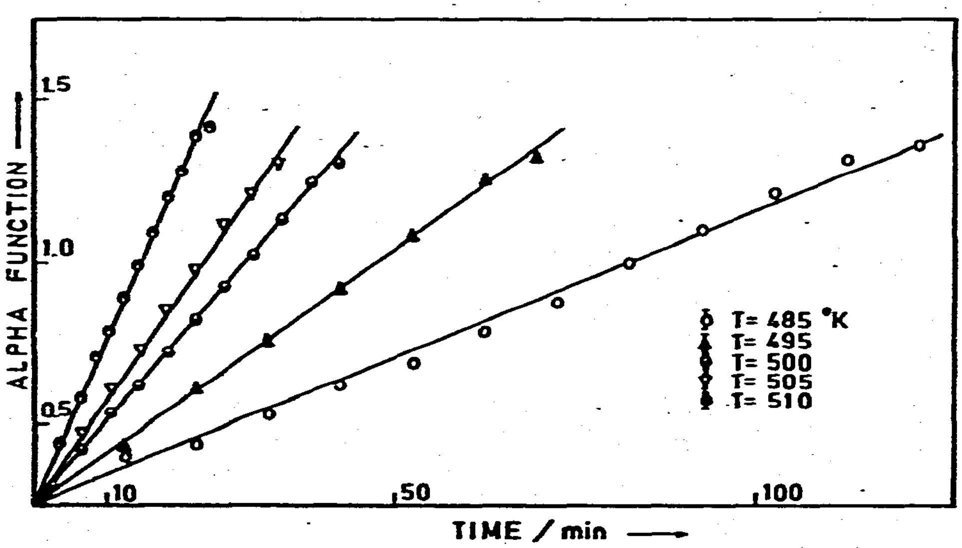

Fig. 1. Plots of $[-\ln(1-\alpha)]^{1/3}$ versus time for the first step of the B4-compound in agreement with the dynamical decomposition pattern in ref. 5.

The activation energies and pre-exponential terms were obtained by means of a least squares fit from Arrhenius plots of the rate constants for the first decomposition step for each compound. These values are listed in Table 1. Fig. 2 shows the family of Arrhenius plots.

TABLE 1

ACTIVATION ENERGIES AND ARRHENIUS PARAMETER FOR THE FIRST DECOMPOSITION STEP FOR THE COMPOUNDS STUDIED

Compound	*Dynamical regime*		*Isothermal regime*	
	Simplified treatment $E(kJ\ mol^{-1})$	*Graphical method* $E(kJ\ mol^{-1})$	*Energy of activation* $E(kJ\ mol^{-1})$	*Arrhenius parameter* (min^{-1})
BP	25.6	83.6	126.8	4.2×10^{11}
B2	15.7	50.2	134.6	7.1×10^{12}
B3	19.3	52.3	132.6	2.7×10^{12}
B4	20.3	53.1	130.4	8.6×10^{11}

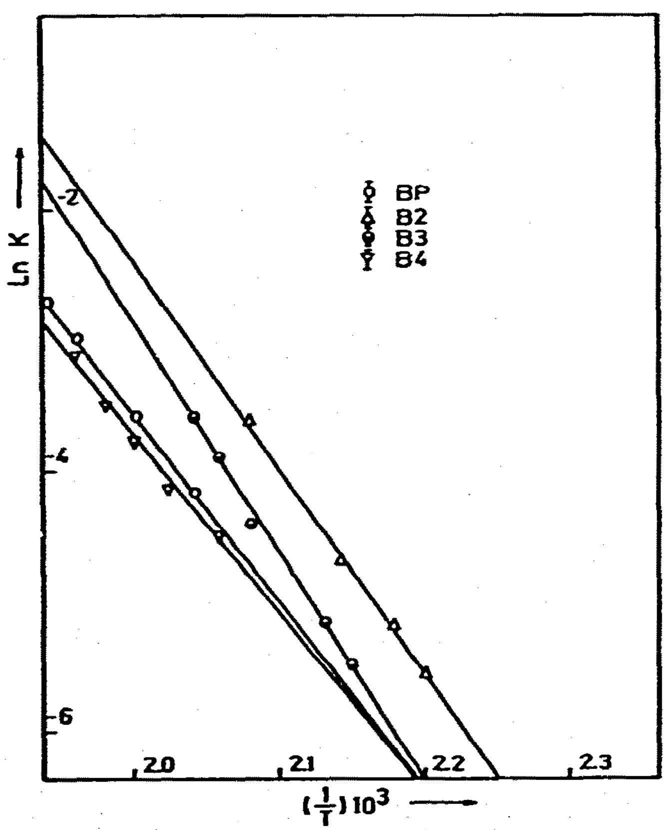

Fig. 2. Arrhenius plots for the compounds studied in dry nitrogen atmosphere.

In a previous communication[5] about the decomposition of these compounds in a dynamical regime the estimation of the activation energy was made with a simplified treatment by means of Satava's analysis[8] and the values found (Table 1) were considerably lower than those found by means of an isothermal method. This is not surprising if we take into account the variations in the apparent activation enthalpy presented in refs. 4 and 9 as a function of the experimental conditions for the thermal decomposition of calcium carbonate. These variations are considerably higher than those found by the authors[1] for calcium oxalate. On the other hand, it seems clear that the kinetic parameters depend on effects such as mass and thermal transfer as well as on the thermal conductivity. In this way the isothermal regime presents clear differences with the dynamical regime. Another factor, the induction period observed, can also influence the disagreement between both dynamical and isothermal regimes.

In order to avoid the above-mentioned approximations a new determination of the activation energies was made by using the new values of a found in this work by means of a graphical method—for comparison of both $g(a)$ and $p(x)$ functions[8]. The new energy activation values are also listed in Table 1. These values are higher than those obtained with an approximate method but they are still lower than those obtained with the isothermal method.

Another interesting observation must be made regarding the behaviour of the activation energy as a function of the substituted pyridines. From dynamical regime results, it seems clear that the factors of symmetry and steric effects explain the order of the experimental values while the isothermal results seem to show that this experimental order is related with the pK_a values of the ligands. The last result is in agreement with another study on complexes of the substituted pyridines[10]. A more complete study about this point, including a higher number of organic bases is under way now.

The analysis of the isothermal data for the second decomposition step is complicated by the existence of an overlap between both decomposition

TABLE 2

ACTIVATION ENERGIES AND ARRHENIUS PARAMETER FOR THE SECOND DECOMPOSITION STEP FOR THE COMPOUNDS STUDIED

Compounds	*Dynamical regime*		*Isothermal regime*	
	Simplified treatment E (kJ mol^{-1})	*Graphical method* E (kJ mol^{-1})	*Energy of activation* E (kJ mol^{-1})	*Arrhenius parameter* (min^{-1})
BP	11.2	34.28	282.9	4.6×10^{24}
B2	9.7	9.3	107.2	1.2×10^{8}
B3	9.2	18.0	105.6	6.2×10^{7}
B4	8.8	31.4	101.3	2.0×10^{6}

steps, specially for the BP and B2 compounds. Table 2 shows the activation energy and pre-exponential factor values derived from isothermal runs by means of a processing of experimental data similar to those shown in ref. 4. The difference can be seen between the values for those compounds with overlapping steps and those with two separate ones. In the same table the values derived from dynamical runs and obtained by means of both, approximate and graphical methods are shown. We can say that the isothermal values in Table 2 are not as significative for comparison as those found for the first step.

CONCLUSIONS

The isothermal regime decomposition data are in agreement with the decomposition pattern proposed in ref. 5 for the two decomposition steps for each compound studied.

The dynamical method seems more adequate for a first scanning concerning the stability of the compound and presents a more critical behaviour for elucidating the most probable mechanism.

The kinetic parameter values from an isothermal regime are higher than those from a dynamical one, but the experimental conditions for the first method seem to be nearer to the theoretical suppositions about the mass transfer and thermal conductivity. In any case the uncontrolled nature of the sample must be taken into account in our experimental results.

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