Journal of Thermal Analysis, Vol. 29 (1984) 1131–1137

KINETIC INTERPRETATION OF THE THERMAL DECOMPOSITION OF ANILINIUM OCTAMOLYBDATE AT DIFFERENT HEATING RATE

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(Received April 17, 1984)

It has been shown many times, how difficult it is to discriminate among different kinetic models for the non-isothermal decompositions of solids. In this work non-isothermal decomposition data for the complex decomposition of anilinium octamolybdate at different heating rates have been analyzed taking into account temperature values at the same solid conversion in order to divide the temperature influence from the conversion influence in the kinetic model.

Results for the apparent activation energy factor and kinetic conversion function are given. Nevertheless it has been not possible to assign a simple kinetic model to the decomposition.

Many experimental works have been published on the decomposition of polymetalates of organic bases. These researches show the difficulties of analyzing the kinetic results coming from these decompositions.

Thermogravimetric data obtained under non-isothermal conditions with constant heating rate are usually very difficult to describe by a kinetic equation in this kind of decompositions.

In this field it has been interesting to study the thermal decomposition of anilinium octamolybdate to receive some general information about the thermal decomposition of polymetalates, such as:

$$S_1 \text{ (initial solid)} \rightarrow S_2 \text{ (intermediate solid)} + G \text{ (gases)}$$

in order to discriminate between kinetic models. However, non-stoichiometric relations had been found before for this kind of decomposition [1, 2] and we have been able to show in an earlier work that the thermal decomposition of anilinium octamolybdate dihydrate takes place with the formation of many intermediate products [3, 4], so that the reaction schema could be written like:

S_1 (initial solid) → S_i (solid products) + G_j (gas products)

where $i = 2, \ldots, n$ and $j = 1, \ldots, m$.

A complex reactions scheme is very difficult to analyze in gas solid non-catalytic reactions as has been shown many times [5]. So we have tried to apply a new kinetic analysis of thermogravimetric data [6], at constant conversion rate to obtain kinetic data coming from runs carried out at different heating rates.

This method tries to explain the difference experienced in the kinetic interpretations of isothermal and non-isothermal data by using different kinetic models as it has been shown in an earlier work [7].

One of the most important problems of the non-isothermal kinetic analysis could be, that the temperature and conversion change together and it increases the difficulty to carry out the discrimination between kinetic models.

Experimental

Synthesis procedure and experimental methods have been explained in an earlier work [3]. In this work different experimental runs have been carried out at heating rates of 2.5, 5.0, 40.0, 80.0, and 160.0 deg min^{-1}.

Results and discussion

A. Analysis at constant conversion rates

A differentiation among kinetic models and evaluation of kinetic parameters will be done by using temperature values for the same conversion at different heating rates.

Taking into account kinetic expressions like:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

and supposing the Arrhenius law for the influence of the temperature in the kinetic model:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A \exp -\frac{E}{RT} \; dt \tag{2}$$

where

$$\int_0^t A \exp -\frac{E}{RT} \; dt \simeq \frac{RT^2}{\beta E} A \exp -\frac{E}{RT} \tag{3}$$

and rearranging

$$\frac{\beta}{T^2} \simeq \frac{A}{\frac{E}{R} g(\alpha)} \exp -\frac{E}{RT} \tag{4}$$

expression, which can be linearized:

$$\mathrm{Ln}\,\frac{\beta}{T^2} \simeq \mathrm{Ln}\,\frac{A}{\frac{E}{R}\,g(\alpha)} - \frac{E}{R}\,\frac{1}{T} \tag{5}$$

This means, that a plot of Ln β/T^2 vs. $1/T$ for kinetic data at the same conversion must be a linear plot.

B. Results

In Figure 1 experimental data for the non-isothermal decomposition are shown as $\alpha - T$ values for different heating rates.

Ln β/T^2 vs. $1/T$ were displayed and the slopes, correlation coefficients and origin ordinates are shown in Table 1 for different conversion values.

This data are plotted in Fig. 2 like E/R vs. α. From this figure it can be deduced, that the activation energy depends on the conversion values but for conversion values

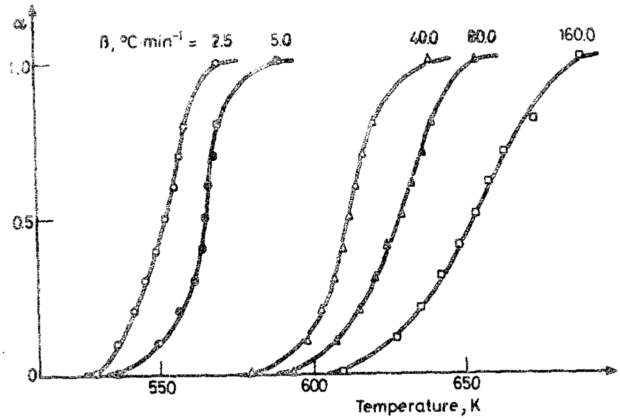

Fig. 1 $\alpha - T$ experimental values at different heating rates

Table 1 Least squares fitting of kinetic data at constant conversion

α	E/R	Ln $A/E/R\,g(\alpha)$	r^2
0.10	14200	14.64	0.996
0.20	14225	14.55	0.998
0.30	14178	14.25	0.997
0.40	14.074	13.92	0.997
0.50	13759	13.24	0.997
0.60	13587	12.83	0.996
0.70	13300	12.22	0.994

between 0.1 to 0.4 an apparent activation energy of $E/R = 14100$ can be given and the dependence of the activation energy with the conversion for highest α values can be explained with a change in the limiting rate step.

It could mean, that from 0.1 to 0.4 conversion values a kinetic reaction mechanism can be the limiting step and from 0.4 to 1.0 conversion values another kinetic mechanism or diffusion can be the controlling step. This change leads to another value for the apparent activation energy factor.

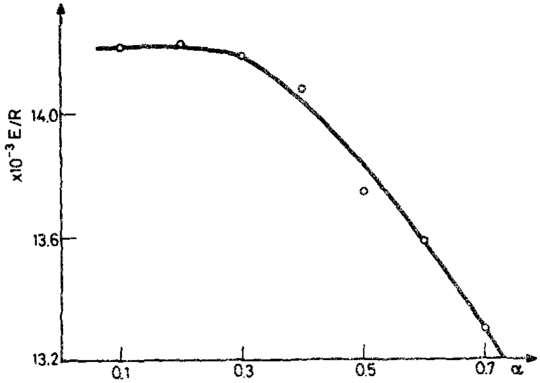

Fig. 2 E/R vs. conversion

C. *Conversion function in the decomposition reaction*

The kinetic analysis of the decomposition data has given a parameter

$$\mathrm{Ln}\,\frac{A}{\frac{E}{R}g(\alpha)}$$

From this value the $g(\alpha)$ function can be obtained.

The $g(\alpha)$ models of different reaction mechanisms used are shown in Table 2. By plotting

$$\mathrm{Ln}\,\frac{A}{\frac{E}{R}g(\alpha)}\ \text{vs.}\ \alpha$$

it is possible to know the $g(\alpha)$ function, in Fig. 3 this function is shown and it is very interesting to see the dependence of $g(\alpha)$ with α, and as can be seen in the representation of the different simple models, it is not possible to explain this dependence by using a simple kinetic model.

Table 2 *Simple kinetic models*

Kinetic model	$f(\alpha)$	$g(\alpha)$	
1. Nucleation and nucleus growing			1.1 $n = \frac{1}{4}$
Kolmogorov, Erofeev, Kazeev, Avrami and Mampel			1.2 $n = \frac{1}{3}$
(KEKAM) equation	$\frac{1}{n}(1-\alpha)(-\text{Ln}(1-\alpha))^{1-n}$	1. $(-\text{Ln}(1-\alpha))^{n}$	1.3 $n = \frac{1}{2}$
			1.4 $n = \frac{2}{3}$
			1.5 $n = 1$
2. Phase boundary reaction	$(1-\alpha)^{1-(1/F_p)}$	2.1 $1-(1-\alpha)$	plane symmetry
		2.2 $1-(1-\alpha)^{1/2}$	cylindrical symmetry
		2.3 $1-(1-\alpha)^{1/3}$	spherical symmetry
3. Diffusion	3.1 α^{-1}	3.1 α^{2}	plane symmetry
	3.2 $(-\text{Ln}(1-\alpha))^{-1}$	3.2 $(1-\alpha)\,\text{Ln}(1-\alpha)+\alpha$	cylindrical symmetry
	3.3 $((1-\alpha)^{1/3}-1)^{-1}$	3.3 $\frac{3}{2}(1-\frac{2}{3}\alpha-(1-\alpha))^{2/3}$	spherical symmetry
4. Potential law	$\frac{1}{n}\alpha^{1-n}$	4. α^{n} $(0 < n < 2)$	4.1 $n = \frac{1}{4}$
			4.2 $n = \frac{1}{3}$
			4.3 $n = \frac{1}{2}$
5. Reaction order	$\frac{1}{n}(1-\alpha)^{1-n}$	5.1 $1-(1-\alpha)^{2}$	order 2
		5.2 $1-(1-\alpha)^{3}$	order 3

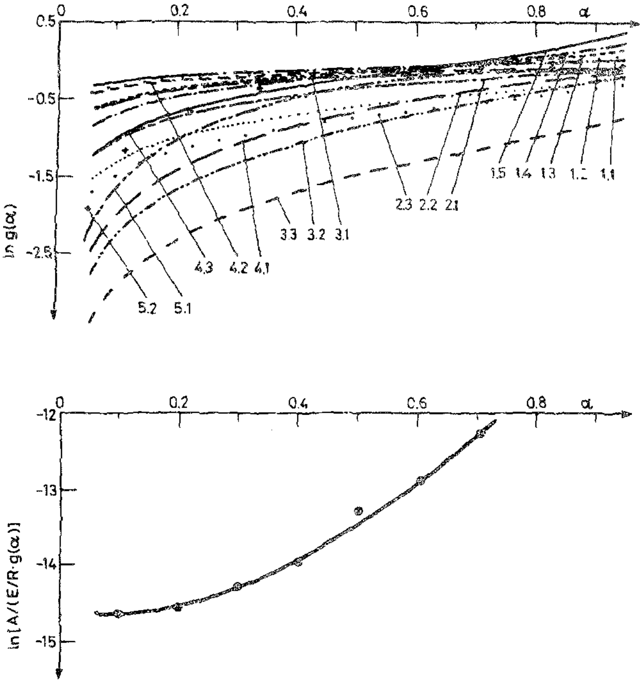

Fig. 3 Ln $E/R/A$ + Ln $g(\alpha)$ vs. α and Ln $g(\alpha)$ vs. α for different kinetic models

Conclusions

The complex thermal decomposition of anilinium octamolybdate has been studied in order to know the possibility to differentiate among commonly used simple kinetic models.

In order to carry out the discrimination a separation of temperature influence and conversion influence has been done.

The dependence of the kinetic parameters on the temperature shows an apparent activation energy factor $E/R = 14100$, from 0.1 to 0.4 of conversion at higher conversion values this activation energy factor decreases.

The kinetic model $g(\alpha)$ function has been plotted against α but it has not been possible to fit the $g(\alpha)$ function to a simple kinetic model. Two different explanations can be made: a) the complex reactions scheme, which is taking place, b) the reaction can be taking place in an interval between chemical reaction control and diffusion control, both explanations lead to complex kinetic models.

These complex kinetic models would be the explanation of the different results obtained under isothermal and non-isothermal conditions [6].

However, in this work we have been able to point out the possibility to use the conversion constant analysis for runs at different heating rates in order to know the real mechanisms of complex thermal decompositions. This method can help very much to understand the kinetic behavior of complex thermal decompositions.

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Zusammenfassung — Es ist oft gezeigt worden, daß es schwierig ist, für nicht-isotherme Zersetzungen von Festkörpern unter verschiedenen kinetischen Modellen das entsprechende auszuwählen. In der vorliegenden Arbeit wurden die für die komplexe nicht-isotherme, bei unterschiedlichen Aufheizgeschwindigkeiten ausgeführte Zersetzung von Anilinium-octamolybdat erhaltenen Daten analysiert, wobei die Temperaturwerte bei gleicher Konversion berücksichtigt wurden, um im kinetischen Modell den Einfluß der Temperatur auf die Konversion auszuschalten. Die scheinbare Aktivierungsenergie und die kinetische Konversionsfunktion sind angeführt, jedoch war es nicht möglich, ein einfaches kinetisches Modell für die untersuchte Zersetzungsreaktion anzugeben.

Резюме — Неоднократно указывалось на трудность распознавания различных кинетических моделей неизотермического разложения твердых тел. В представленной работе проанализированы данные неизотермического разложения анилиний октамолибдата при различных скоростях нагрева, учитывая значения температуры при том же самом превращении твердого тела с целью разделить температурный эффект конверсионного влияния в кинетической модели. Приведены результаты определения кажущегося коэффициента энергии активации и кинетическая функция превращения. Вместе с тем не представилось возможным определить простую кинетическую модель разложения.