KINETIC ANALYSIS OF THERMAL DECOMPOSITION OF PRASEODYMIUM(III) NITRATE HEXAHYDRATE

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The kinetics of thermal decomposition of praseodymium(III) nitrate hexahydrate was studied by using isothermal and dynamic thermogravimetric techniques. Kinetic analysis of the isothermal data with respect to various solid-state reaction models showed that the reaction is best described by phase boundary-controlled and random nucleation models. Kinetic analysis of the dynamic TG curves was discussed and a critical comparison was made of two integral methods, that of Coats and Redfern and that of Ozawa. The results showed that the Ozawa method gives a better correlation, and the results are in good agreement with those obtained under isothermal thermogravimetric conditions.

Processes involving the chemical transformations of solids play an increasingly important role in modern technology, as sophisticated and costly solids can be produced by reactions of other precursor solids. To obtain the desired purity in the structure and texture of the material, a very careful control of the reaction is necessary [1].

There is a considerable diversity of mechanisms by which solids react and there are a variety of factors which may control, determine, influence or modify the rate-limiting processes. Depending on the system investigated, the kinetics of thermal decomposition reactions has been followed in many cases by measurements of pressure changes, and by product analysis by mass spectrometry. However, more recently DTA–TG–DTG analytical techniques are more widely used, since they provide a rapid and convenient method for the quantitative investigation of decomposition reactions [2].

Several approaches have been used to calculate the kinetic parameters from the experimental data. A comparison of the fractional reaction (α) *vs.* time curves measured for a particular reaction with the theoretical expressions derived for appropriate nucleation and growth models has been widely used as evidence for the identification of the geometry of interface advance.

Although the theoretical basis of the equations used in the interpretation of dynamic TG data has been questioned in the literature, several examples of close agreement between the results of isothermal and dynamic methods have been reported. Non-isothermal data are dependent on the heating rate and are subject to possible inaccuracies due to the influence of sample size and shape on heat flow, and for these reasons isothermal kinetic measurements are, in general, the more reliable [3].

In the present study, the kinetics of the isothermal and non-isothermal decomposition of praseodymium nitrate hexahydrate crystals was studied, and it was suggested that the product growth is controlled by a phase boundary reaction.

Experimental

The decomposition of praseodymium nitrate hexahydrate was studied by dynamic thermogravimetry TG with Perkin–Elmer TGS–2 and DTA system 7/4 instruments coupled to a System 4 Microprocessor Controller and a 3600 Thermal Analysis Data Station.

The experiments were conducted in nitrogen atmospheres at a flow rate of 10 ml/min, with about 5 mg of sample, which was obtained from Ventron GmbH and used as received.

The kinetics of the thermal decomposition of praseodymium nitrate hexahydrate crystals was investigated by using isothermal and dynamic TG techniques. Isothermal measurements were performed in the temperature range 325° to 345°, so
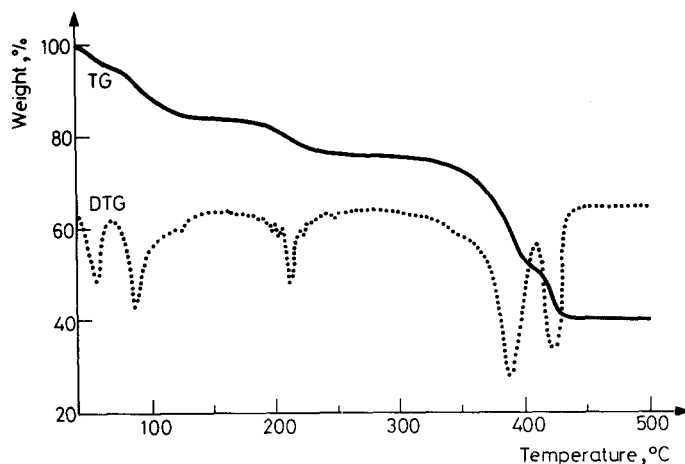

Fig. 1 TG and DTG curves of Praseodymium nitrate hexahydrate at 5 deg min^{-1}
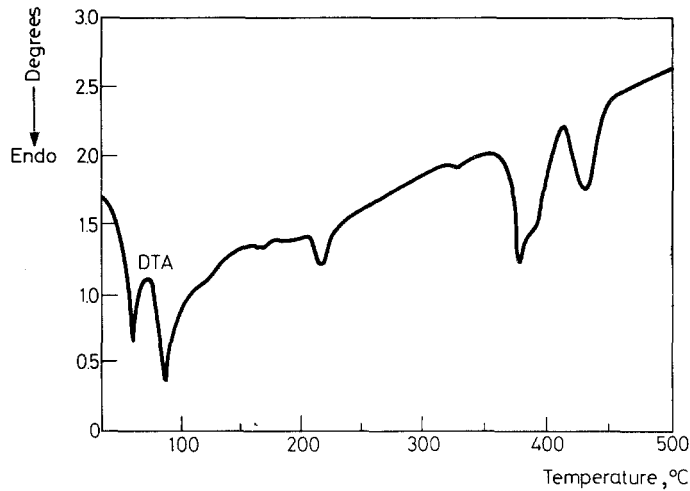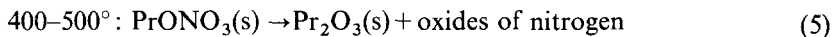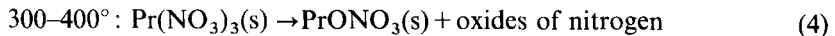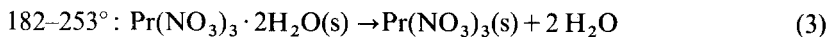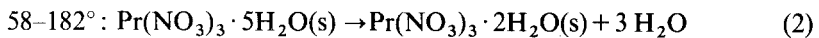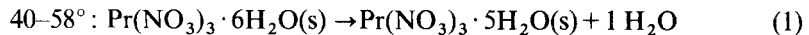
Fig. 2 DTA curve of Praseodymium nitrate hexahydrate at 5 deg min^{-1}

as to ensure linear heating rates and accurate temperature. TG and DTA studies showed that praseodymium nitrate hexahydrate loses weight in several steps. Figures 1 and 2 show the TG, DTG and DTA curves obtained at a heating rate of 5 deg min^{-1}.

The DSC curves were obtained in the same way. Peak integration and subsequent enthalpy calculations were performed by using the Perkin–Elmer System 7/4 partial-area integration program. The melting endotherm of pure indium metal ($\Delta H_f = 28.4$ J/g) was used for calibration.

Results and discussion

The thermal dehydratation takes place through the following scheme:

$$40\text{--}58°: \text{Pr(NO}_3)_3 \cdot 6\text{H}_2\text{O(s)} \rightarrow \text{Pr(NO}_3)_3 \cdot 5\text{H}_2\text{O(s)} + 1\,\text{H}_2\text{O} \qquad (1)$$

$$58\text{--}182°: \text{Pr(NO}_3)_3 \cdot 5\text{H}_2\text{O(s)} \rightarrow \text{Pr(NO}_3)_3 \cdot 2\text{H}_2\text{O(s)} + 3\,\text{H}_2\text{O} \qquad (2)$$

$$182\text{--}253°: \text{Pr(NO}_3)_3 \cdot 2\text{H}_2\text{O(s)} \rightarrow \text{Pr(NO}_3)_3\text{(s)} + 2\,\text{H}_2\text{O} \qquad (3)$$

$$300\text{--}400°: \text{Pr(NO}_3)_3\text{(s)} \rightarrow \text{PrONO}_3\text{(s)} + \text{oxides of nitrogen} \qquad (4)$$

$$400\text{--}500°: \text{PrONO}_3\text{(s)} \rightarrow \text{Pr}_2\text{O}_3\text{(s)} + \text{oxides of nitrogen} \qquad (5)$$

It is evident from the TG and DTG curves (Fig. 1) that the dehydration of $\text{Pr(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ crystals takes place in three steps. The DTG curves exhibits three maxima, at 50, 85 and 214°, in good agreement with the three changes of slope in the

TG curve, at 40–58, 58–182 and 182–253°. The weight losses corresponding to the above effects are due to the liberation of one, three and two water molecules, respectively.

The TG trace of $Pr(NO_3)_3 \cdot 6H_2O$ indicates that the anhydrous compound is formed at 253°. Anhydrous $Pr(NO_3)_3$ is stable over the wide temperature range of 253–300°.

Decomposition begins at 310° and is a two-stage process below 500°. The first stage occurs in the temperature interval 310–395° and gives $PrONO_3$ as degradation product. The second stage takes place in the temperature interval 420–500° and is associated with degradation to Pr_2O_3. The corresponding weight losses are 50.1% (calculated, 50.32%) and 37.8% (calculated, 37.9%), respectively.

The dehydration and decomposition of the investigated compound were also observed from the DTA and DSC curves (Fig. 2). A first endotherm at 60°, which corresponds to the loss of one molecule of water ($\Delta H = 28.2$ kJ mol^{-1}) is followed by two other endotherms, at 86° and 216°, attributed to the loss of three and two molecules of water ($\Delta H = 73.7$ kJ mol^{-1} and 46.0 kJ mol^{-1}), respectively. The final endothermic peaks correspond to the decomposition of anhydrous praseodymium nitrate. This decomposition is evidenced by a small effect at 327°, followed by a large peak at 379°, with a small shoulder to its right (400°), which indicates the formation of $PrONO_3$ ($\Delta H = 158.0$ kJ mol^{-1}), and another at 431°, attributed to degradation to Pr_2O_3 ($\Delta H = 65.1$ kJ mol^{-1}).

Figure 3 shows typical α vs. t curves for the isothermal decomposition of praseodymium nitrate hexahydrate. Under isothermal conditions, the rate constant K is independent of reaction time, and so $Kt = g(\alpha)$. A plot of $g(\alpha)$ vs. time should
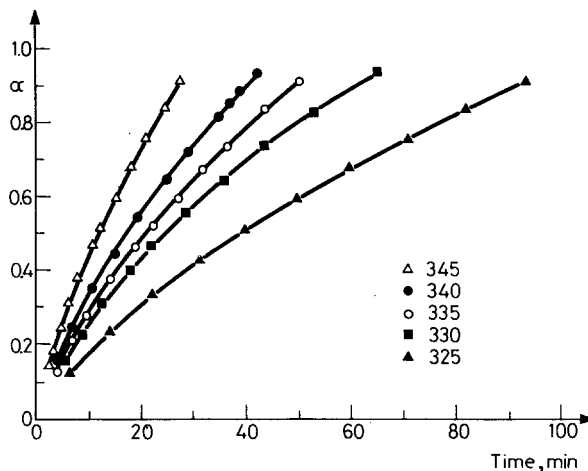

Fig. 3 Isothermal α/t curves for decomposition of $Pr(NO_3)_3 \cdot 6H_2O$ at different temperatures

Table 1 Kinetic equations examined in this work

Reaction model	$g(\alpha)$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2
Jander equation, three-dimensional diffusion	$(1-(1-\alpha)^{1/3,2}$	D_3
Ginstling–Brounshtein equation, three-dimentional diffusion	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$(1-(1-\alpha)^{1/2})$	R_2
Three-dimensional phase boundary reaction	$(1-(1-\alpha)^{1/3})$	R_3
First-order kinetics	$(-\ln(1-\alpha))$	F_1
Random nucleation: Avrami equation	$(-\ln(1-\alpha))^{1/2}$	A_2
Random nucleation: Erofeev equation	$(-\ln(1-\alpha))^{1/3}$	A_3

therefore give a straight line if the correct form of $g(\alpha)$ is used. Table 1 lists some of the more important kinetic equations given in the literature [4, 5], which were examined in the present study in order to find the most appropriate kinetic expression and reaction model which describe the reaction.

The function $g(\alpha)$ depends on the mechanism controlling the reaction and on the size and shape of the reacting particles.

In diffusion-controlled reactions, D_1 denotes a one-dimensional diffusion process governed by a parabolic law, with a constant diffusion coefficient; D_2 is a two-dimensional diffusion-controlled process in a cylinder; D_3 is Jander's equation for a diffusion-controlled reaction in a sphere; and D_4 is the function for a diffusion-controlled reaction starting on the exterior of a spherical particle.

If the reaction is controlled by the movement of an interface at constant velocity and nucleation occurs virtually instantaneously, then for such phase boundary-controlled reactions relating α and t we have the function R_2 for a circular disc reacting from the edge inwards, and function R_3 for a sphere reacting from the surface inwards. If the solid-state reaction follows first-order kinetics (function F_1), then the rate-determining step is the nucleation process and there is an equal probability of nucleation at each active site. In phase boundary reactions, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particle is covered with a layer of product. Nucleation of the reactant, however, may be a random process, not followed by rapid surface growth. As the nuclei grow larger, they must eventually impinge on one another, so that growth ceases where they touch. This process has been considered by Avrami and by Erofeev, who have given functions A_2 and A_3, respectively.

The isothermal α vs. t data were analyzed according to the various kinetic equations by regression analysis, and the comparison given in Table 2 shows that

Table 2 Comparison of fits of various kinetic models to the isothermal results on the thermal decomposition of praseodymium nitrate

Function symbol	Temperature, °C				
	325	330	335	340	345
D_1	0.8884	0.9985	0.9978	0.9964	0.9977
D_2	0.9915	0.9932	0.9924	0.9910	0.9910
D_3	0.9655	0.9826	0.9871	0.9813	0.9772
D_4	0.9887	0.9899	0.9893	0.9881	0.9869
R_2	0.9999	0.9994	0.9998	0.9994	0.9994
R_3	0.9996	0.9996	0.9996	0.9991	0.9989
F_1	0.9965	0.9978	0.9974	0.9969	0.9955
A_2	0.9991	0.9976	0.9989	0.9989	0.9986
A_3	0.9967	0.9943	0.9967	0.9969	0.9966

the best fit of the data is obtained with phase boundary-controlled reactions (functions R_2 and R_3). For the R_2 model, typical plots of $(1 - (1 - \alpha)^{1/2})$ vs. time in the temperature range 325° to 345° are shown in Fig. 4. The rate constants estimated from the slopes of these curves were used to calibrate the Arrhenius parameters.

Figure 5 shows representative weight changes as a function of temperature from dynamic measurements on $Pr(NO_3)_3 \cdot 6H_2O$ thermal decomposition. In the analysis of the dynamic TG curves, we assumed function R_2 (which gave the highest correlation coefficient) and made a critical comparison of two integral methods, that of Coats and Redfern [6, 7] and that of Ozawa [8].
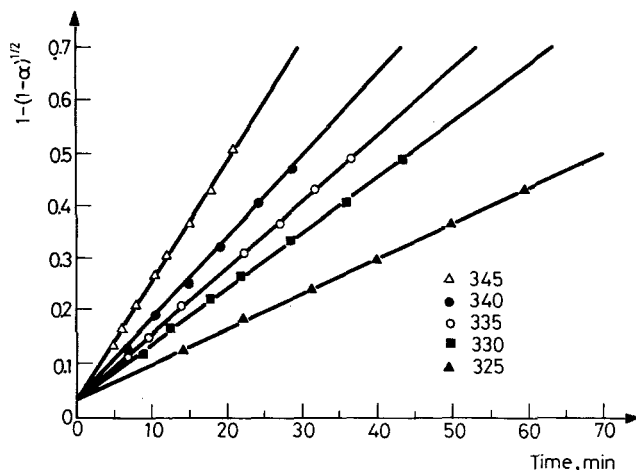
Fig. 4 Isothermal decomposition of $Pr(NO_3)_3 \cdot 6H_2O$, according to the two dimensional phase-boundary reaction model at different temperatures

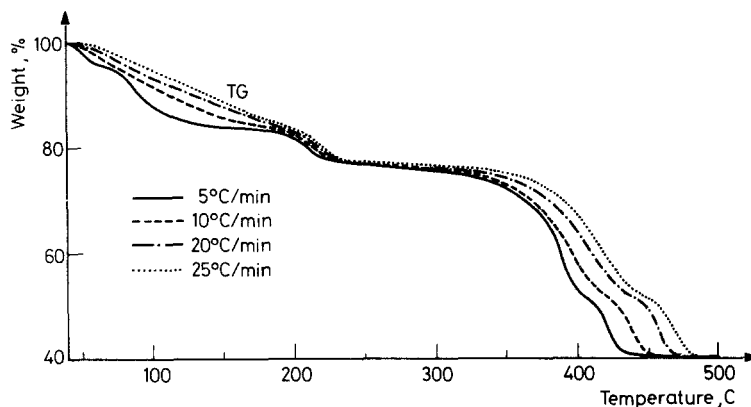**Fig. 5** Typical weight changes from dynamic measurements for $Pr(NO_3) \cdot 6H_2O$ thermal decomposition, at different heating rate

In the Coats and Redfern method, for the calculation of the activation energy, the correct form of $g(\alpha)$ is used in the equation:

$$-\ln g(\alpha)/T^2 = -\ln (AR/\beta E)(1 - 2RT/E) + (E/RT)$$

where β is the rate of temperature change, and the quantity $\ln (AR/\beta E)(1 - 2RT/E)$ appears to be reasonably constant for most values of E and the temperature range over which most reactions occur. In the Ozawa approximate integral method, a master curve may be derived from the thermogravimetric data obtained at different heating rates, and the result is:

$$AE/R\beta_1 P(E/RT_1) = AE/R\beta_2 P(E/RT_2) = \ldots$$

where the function $P(E/RT)$ was approximated via the equation:

$$\log P(E/RT) = -2.315 - 0.4567(E/RT)$$

Hence, the activation energy was calculated from the thermogravimetric curves obtained at different heating rates. The frequency factor was determined by subtracting $\log (E/\beta R)P(E/RT)$ from $\int d(1 - \alpha)/f(1 - \alpha)$ determined from $f(1 - \alpha)$. Table 3 shows the results of calculation of the kinetic parameters for these three methods, assuming that the reaction obeys the R_2 model.

Sharp and Wentworth [7] made a comparative study between differential methods and the Coats and Redfern integral method in studying the decomposition of $CaCO_3$, and concluded that the Coats and Redfern method leads to a more satisfactory kinetic analysis.

The results obtained in the present study show that the Ozawa method gives a more satisfactory kinetic analysis than that of Coats and Redfern. The correlation

Table 3 Kinetic parameters for R_2 model calculated according to isothermal and dynamic methods

Method of analysis	Heating rate, deg min^{-1}	E, kJ mol^{-1}	ln A, min^{-1}	Correlation coefficient
Isothermal		174.9	30.2	0.990
Dynamic				
a) Coats and Redfern	5	185.4	23.2	0.997
	10	195.5	25.0	0.997
	20	273.3	39.0	0.999
	25	257.3	35.0	0.998
b) Ozawa		164.0	28.0	

coefficient depended to a large extent on the number of data points taken in the regression analysis. We have used data points covering the range $0.15 < \alpha < 0.9$.

The Coats and Redfern method is less tedious to apply to the TG data than the direct differential method because it avoids the determination of tangents, but the results obtained are still not accurate enough and do not compare well with the results of isothermal kinetic analysis.

On the other hand, the Ozawa method of analysis gave more accurate results and better agreement with the results of isothermal TG kinetic analysis.

In this study we have used a computer program (IBM, PC–AT). A single activation energy and frequency factor are obtained instead of a wide range of values obtained at different heating rates. It allows comparisons between different dynamic results obtained under different conditions.

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Zusammenfassung — Mittels isothermer und dynamischer thermogravimetrischer Methoden wurde die Kinetik der thermischen Zersetzung des Hexahydrates von Praseodymnitrat untersucht. Eine kinetische Auswertung der isothermen Meßdaten unter Anwendung verschiedener Feststoffreaktionsmodelle ergab, daß die Reaktion am besten durch ein phasengrenzenkontrolliertes Randomkeimbildungsmodell beschrieben werden kann. Die kinetische Auswertung der dynamischen TG-Kurven wurde diskutiert und ein kritischer Vergleich zwischen zwei Integriermethoden, der von Coats und Redfern und der von Ozawa, angestellt. Die Betrachtungen ergaben, daß die Methode von Ozawa eine bessere Korrelation liefert und daß die Resultate gut mit denen der isothermen thermogravimetrischen Messungen übereinstimmen.

Резюме — Методом изотермической и динамической термогравиметрии изучена кинетика термического разложения гексагидрата нитрата празеодима. Кинетический анализ изотермических данных, проведенный с использованием различных моделей твердотельных реакций, показал, что реакция наилучшим образом описывается моделью контролируемой межфазовой границы и моделью произвольного образования центров кристаллизации. Обсужден кинетический анализ динамических кривых ТГ и проведено критическое сопоставление интегральных методов Коуэтса–Рэдферна и Озавы. Результаты показали, что метод Озавы дает лучшую корреляцию и результаты хорошо согласуются с данными, полученными методом изотермической термогравиметрии.