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Journal of Nuclear Materials 252 (1998) 28–33

journal of nuclear materials

Kinetic study of the thermal decomposition of thorium oxalate dihydrate

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Received 2 May 1996; accepted 8 October 1997

Abstract

In this study, the thermal decomposition of thorium oxalate dihydrate ($Th(C_2O_4)_2 \cdot 2H_2O$) is investigated by using thermogravimetry, differential thermal analysis techniques (TGA-DTA). The specific surface area measurements between 100–900°C are used for the demonstration of the number of steps of thorium oxalate dihydrate's thermal decomposition. The kinetic parameters are calculated by Coats' method. © 1998 Elsevier Science B.V.

1. Introduction

It is well known that thorium oxalate is a starting material for the purpose of obtaining thorium dioxide, which is then to be used as a nuclear fuel in nuclear reactors since it gives birth to ^{233}U, which is a fissile element, by neutron bombardment. Thorium dioxide can be obtained by calcination of thorium oxalate in air atmosphere [1]. TGA-DTA show that this happens in several decomposition steps.

There is enough work reported on this subject. However, there were usually disagreements on the decomposition steps. Various thorium oxalate containing one to seven molecules of water were reported. Depending on the number of molecules of water there were alterations. This was one aspect of disagreement. However, there were also different points of view between the researchers experimenting with thorium oxalate containing the same water of crystallization, due to the decomposition of carbonate groups.

These differences in opinion have indicated a need for more studies on the thermal decomposition of thorium oxalate. In this study, thorium oxalate's thermal decomposition and decomposition steps are investigated by using TGA-DTA and by measuring thorium oxalate's surface area at different temperatures. The kinetic parameters for each step are calculated by Coats's method [2].

2. Theory

TGA-DTA techniques have been used for determining decomposition temperatures and decomposition steps.

The kinetic measurement are established by COATS'method [2]. In the reaction

$$aA_{(s)} \rightarrow bB_{(s)} + cC_{(g)},$$

the rate of disappearance of A may be expressed by

$$\frac{d\alpha}{dt} = k(1-\alpha)^n, \qquad (1)$$

where α is the fraction of A decomposed at time t, n is the order of reaction and k is the rate constant given by the expression

$$k = Ae^{-E/(RT)}, \qquad (2)$$

where A is the frequency factor, and E is the activation energy of the reaction. A is considered for gases and liquids as frequency factor and is proportional to the number of successful collisions of the reacting molecules.

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PII S0022-3115(97)00318-8

Solid particles are not free to move and A can be considered as a preexponential constant [3].

For linear heating rate of, say, a $\mathrm{deg\,min}^{-1}$,

$$a = \frac{\mathrm{d}T}{\mathrm{d}t}. \tag{3}$$

Combining Eqs. (1)–(3), rearranging and integrating, we get

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \frac{A}{a} \int_0^T \mathrm{e}^{-E/(RT)} \mathrm{d}T. \tag{4}$$

The right-hand side of Eq. (4) has no exact integral, but by making the substitution $u = E/(RT)$ and using the relation

$$\int_u^{\infty} \mathrm{e}^{-u} u^{-b} \mathrm{d}u \simeq u^{1-b} \mathrm{e}^{-u} \sum_{n=0}^{\infty} \frac{(-1)^n (b)^n}{u^{n+1}}.$$

Eq. (4) becomes

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{aE}\left[1 - \frac{2RT}{E}\right] \mathrm{e}^{-E/(RT)} \tag{5}$$

taking logs

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT} \tag{6}$$

for all values of n except $n = 1$ in which case Eq. (4), after taking logs, becomes

$$\log_{10}\left[-\log_{10}\frac{(1-\alpha)}{T^2}\right] = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT}. \tag{7}$$

Thus a plot of either

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \text{ against } \frac{1}{T}$$

or, where $n = 1$,

$$\log_{10}\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right] \text{ against } \frac{1}{T} \tag{8}$$

should result in a straight line of slope $-E/2.3R$ for the correct value of n, since it may be shown that, for most values of E and for the temperature range over which reactions generally occur, the expression

$$\log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]$$

is sensibly constant. In that case, Eqs. (6) and (7) can be written as $y = ax + b$:

$$b = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right], \qquad x = \frac{1}{T}, \qquad a = -\frac{E}{2.3R}.$$

E and A can be calculated from the slope and the intercept.

3. Experimental

The thorium oxalate dihydrate is prepared by adding 0.5 M oxalic acid solution drop by drop (10 $\mathrm{cm}^3/\mathrm{min}$) to the 0.5 M commercial thorium nitrate solution under stirring (100 rpm) at room temperature. After adding the total stoichiometric amount of oxalic acid, the precipitate which is kept for 1 h for the digestion, is filtrated using Whatmann 42 filter paper and washed by warm water until oxalate ions are present in the filtrate and is dried at 100°C in the dryer for 24 h.

Shimadzu Thermal Analysis System is used for TGA-DTA experiments. The starting sample amount for TGA is 130.12 mg. The heating rate is 5°C/min and the upper limit of the temperature is 800°C. The DTA study is made under the same conditions. 53.4 mg of the mass is lost in air atmosphere. This means that the mass loss which occurred between the starting and the ending material is 41%.

X-ray diffraction peaks are obtained by a Philips X-ray diffractometer using Cu Kα radiation.

Specific surface area measurements are made by micromeritics high speed surface area analyzer using BET method. Oxalate samples are heated at 100°C for 1 h and oxide samples at 300°C for 40 min for degassing operation before the surface area measurements.

The determination of the impurities of commercial thorium nitrate and thorium oxalate is made by ICP-OES (inductively coupled plasma-optical emission spectrometry) technique (Table 1).

4. Result and discussions

The result that 41% of the mass loss occurred between the start and the end material (Fig. 1) and X-ray diffrac-

Table 1

Impurities in thorium nitrate and thorium oxalate dihydrate

	Impurities (ppm)	
	thorium nitrate	thorium oxalate dihydrate
Cd	24	17
Mn	13	9
Cr	15	9.53
Cu	710	45
Na	18	75
K	2.4	2.4
Ca	126	117
Mg	10	10.3
Fe	11	8.5
Zn	41	26

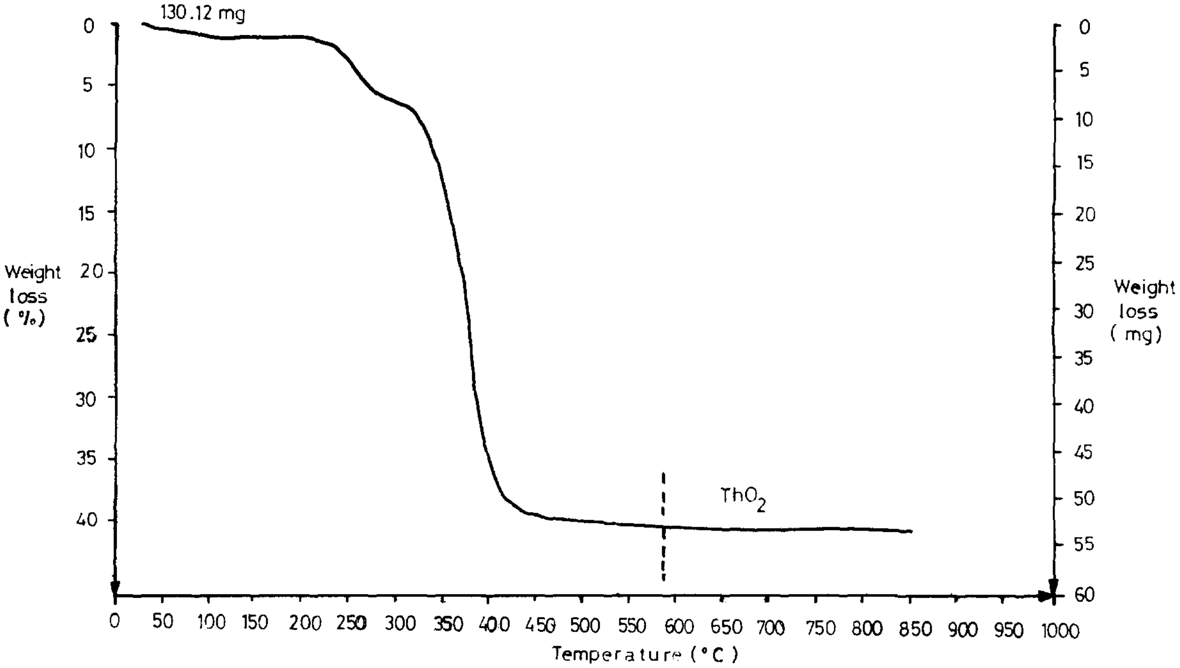

Fig. 1. Thermogravimetry of thorium oxalate in air atmosphere.

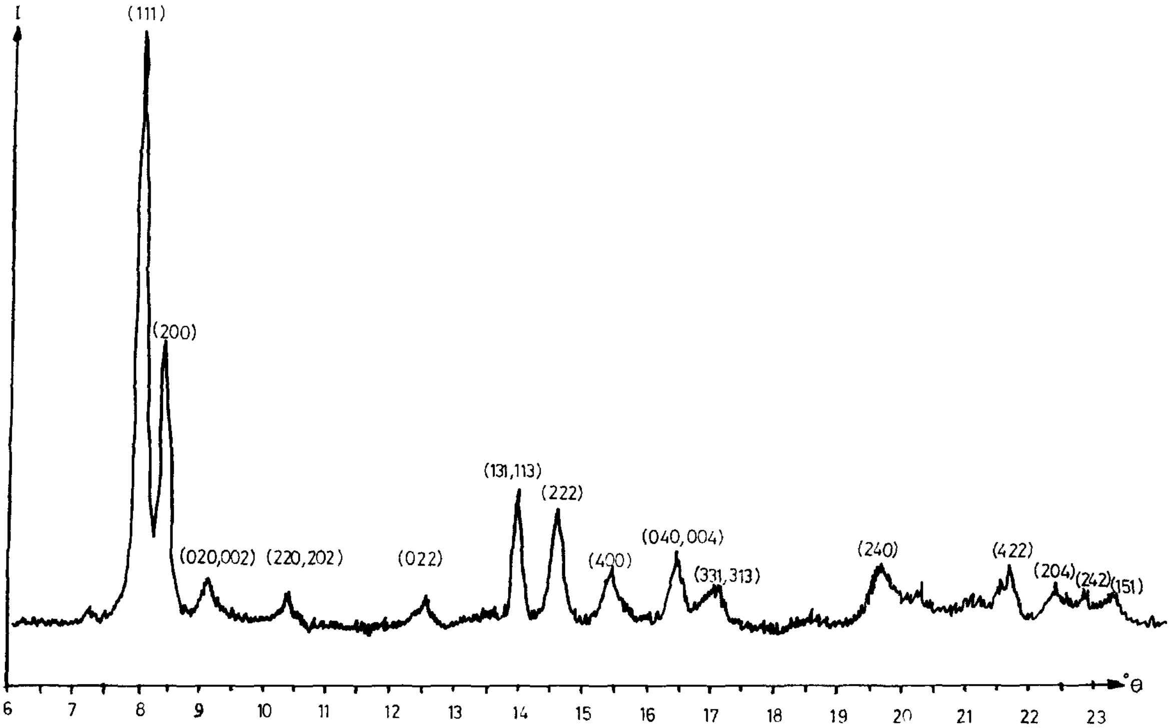

Fig. 2. X-ray diffractometer peaks of $Th(C_2O_4)_2 \cdot 2H_2O$.

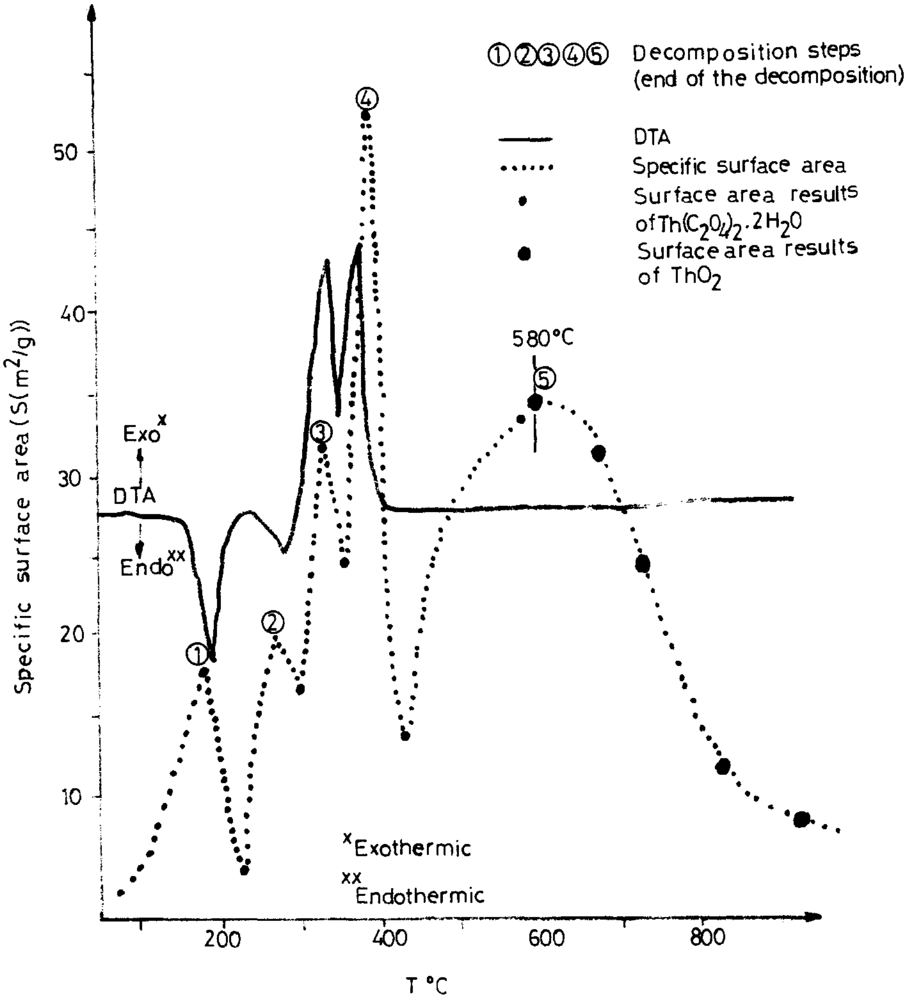

Fig. 3. DTA and specific surface area of Th(C$_2$O$_4$)2 · 2H$_2$O.

tometer peaks (Fig. 2) both indicate that thorium oxalate contains 2 moles of water of crystallization. The number of slopes and peaks in the TGA (Fig. 1) and DTA (Fig. 3) curves, respectively, show the steps of thermal decomposition of thorium oxalate dihydrate.

For the first time, in this study, the surface area measurement between 100–900°C are used for the demonstration of the number of steps of the thermal decomposition of $Th(C_2O_4)_2 \cdot 2H_2O$.

In the literature, there are a number of studies on this subject. According to Kinoshita et al. [4], thorium oxalate dihydrate decomposes in two steps:

Step 1: $Th(C_2O_4)_2 \cdot 2H_2O \xrightarrow{-H_2O} Th(C_2O_4)_2 \cdot H_2O$

Table 2
Decomposition temperatures of the reactions and comparison with Padmanabhan et al.'s results

Decomposition reactions	This study (°C)	Ref. [5] (°C)
$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$	180	140
$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$	280	260
$Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO_2 + 2CO$	–	360
$Th(ClO4)_2 \rightarrow Th(CO_3)_2 + 2CO$	340	–
$Th(CO_3)_2 \rightarrow ThOCO_3 + CO_2$	390	–
$ThOCO_3 \rightarrow ThO_2 + CO_2$	410	–

Table 3
Kinetic parameters of decomposition reactions

Decomposition reactions	Reaction order	Activation energy[a]
$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$	0.5	32
$TH(C_2O_4)_2 \cdot H_2O \rightarrow TH(C_2O_4)_2 + H_2O$	0.33	33
$Th(C_2O_4)_2 \rightarrow Th(CO_3)_2 + 2CO$	1.5	99
$TH(CO_3)_2 \rightarrow THOCO_3 + CO_2$	1.5	235.5
$ThOCO_3 \rightarrow ThO_2 + CO_2$	2	33.5

[a] kcal mol^{-1}.

$$\text{Step 2: } Th(C_2O_4)_2 \cdot H_2O \xrightarrow{-H_2O} Th(C_2O_4)_2$$
$$\rightarrow ThO_2 + 2CO + 2CO_2.$$

Padmanabhan et al. [5] have observed three peaks in their DTA curve:

$$\text{Step 1: } Th(C_2O_4)_2 \cdot 2H_2O \xrightarrow{-H_2O} Th(C_2O_4)_2 \cdot H_2O$$
$$\text{Step 2: } Th(C_2O_4)_2 \cdot H_2O \xrightarrow{-H_2O} Th(C_2O_4)_2$$
$$\text{Step 3: } Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO + 2CO_2.$$

For the first time, D'Eye and Sellman [6] have revealed the existence of the intermediate carbonate products during the thermal decomposition of oxalates. They have demonstrated that the decarbonation of thorium oxalate has occurred as follows:

$$Th(C_2O_4)_2 \rightarrow Th(CO_3)_2 + 2CO$$
$$Th(CO_3)_2 \rightarrow ThO_2 + 2CO_2.$$

According to the DTA curve (Fig. 3) of this study, $Th(C_2O_4)_2 \cdot 2H_2O$'s decomposition occurs in four steps. This result is in agreement with that of D'Eye and Sellman. The first two endothermic peaks are due to the loss of water crystallization. The other two exothermic peaks are due to the decarbonation. However, more studies on the weight loss calculations and on the surface area results, have revealed the existence of the additional intermediate carbonate compound corresponding to $ThOCO_3$. The existence of this type of carbonation product was demonstrated by Turcotte et al. [7] in their study on the rare earth dioxymonocarbonates and their decomposition.

Table 4
Activation energies of decomposition reactions and comparison with Padmanabhan et al.'s results[a]

Decomposition reactions	This study	Ref. [5]
$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$	32	26
$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$	33	36
$Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO_2 + 2CO$	–	55
$Th(C_2O_4)_2 \rightarrow Th(CO_3)_2 + 2CO$	99	–
$Th(CO_3)_2 \rightarrow ThOCO_3 + CO_2$	235.5	–
$ThOCO_3 \rightarrow ThO_2 + CO_2$	33.5	–

[a] kcal mol^{-1}.

Normally, when the temperature is increased, the surface area of the stable material decreases. In this case, thorium oxalate dihydrate decomposes, between 100–580°C, to thorium dioxide which is the stable material. During the thermal decomposition of thorium oxalate to thorium dioxide, the surface area results have showed some peaks (Fig. 3). This anomaly is caused by the steps of the decomposition. It can be observed from the surface area–temperature curve that there are five decomposition steps:

$$Th(C_2O_4)_2 \cdot 2H_2O \xrightarrow{-H_2O} Th(C_2O_4)_2 \cdot H_2O + H_2O$$
$$Th(C_2O_4)_2 \cdot H_2O \xrightarrow{-H_2O} Th(C_2O_4)_2 + H_2O$$
$$Th(C_2O_4)_2 \rightarrow Th(CO_3)_2 + 2CO$$
$$Th(CO_3)_2 \rightarrow ThOCO_3 + CO_2$$
$$ThOCO_3 \rightarrow ThO_2 + CO_2.$$

$ThOCO_3$ decomposition could not be determined by DTA because the decomposition temperature of $Th(CO_3)_2$ and $ThOCO_3$ are very close (390–410°C) (Fig. 3, Table 2). It will be seen in the section about calculation of the activation energies that the activation energy of $Th(CO_3)_2$ is very high according to $ThOCO_3$'s activation energy (Table 3). In DTA, this two decompositions may be characterized together.

Kinetic parameters calculated in this study are resumed in Table 3. The results are compared with Padmanabhan et al.'s result in Table 4. Calculations are made for each decomposition step using n values: $n = 0$, $n = 0.33$, $n = 0.5$, $n = 0.67$, $n = 1$, $n = 1.5$, $n = 2$ and the highest correlation coefficient is chosen for the determination of the apparent reaction order.

5. Conclusion

In conclusion, thermal decomposition of thorium oxalate dihydrate has occurred in a few steps as determined in Section 4.

Kinetic parameters are calculated using Coats' method. The loss of the water crystallization's activation energy results are in good agreement with the literature. However, for the other steps, there are different points of view.

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