

## **THERMAL DECOMPOSITION KINETICS OF THORIUM(IV) CHELATES OF TWO NAPHTHOL DYES**

*S. Vatsala and G. Parameswaran\**

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALICUT, KERALA, INDIA 673 735

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The thermal decomposition of thorium(IV) chelates of 1-(2-fluorenylazo)-2-naphthol and *o*-carboxyphenylazo-2-naphthol was studied by TG. Thermoanalytical data (TG and DTG) of these chelates are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction, the energy and entropy of activation based on the differential method employing the Freeman–Carroll equation, the integral method using Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are also given. On the basis of experimental findings in the present course of studies the relative thermal stabilities of the thorium chelates can be given as  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2] > [\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ .

Very few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating agents [1]. Wendlandt [2–5] and Hill [6, 7] studied the thermal properties of metal chelates with different types of complexing ligands. Studies on thermal decomposition and kinetics of metal chelates with azo and azomethine ligands have been done by a few workers [8–12]. In continuation of our work [13] on thermal decomposition kinetics of metal chelates, we report in this paper, the thermal stability and kinetic parameters of thorium(IV) chelates of two novel azo dyes.

### **Experimental**

Samples of thorium(IV) chelates of 1-(2-fluorenylazo)-2-naphthol and *o*-carboxyphenylazo-2-naphthol were prepared by adding aqueous solutions of  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  to DMSO solutions of the respective dye ligands in 1 : 2 ratio in presence of a few drops of dilute ammonium hydroxide and heating on a water bath for one hour. The precipitates were filtered, washed with an aqueous solution of

DMSO and dried in vacuum desiccator. The purity of the samples was checked by elemental analysis for the metal and C, H, N analysis. The structures of these two chelates were found [14] to be  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  and  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ .

### Apparatus

A Stanton recording thermobalance Model TR-1 was used for recording TG traces. The heating rate was 5 or 6  $\text{deg min}^{-1}$  and chart speed was 6 in  $h^{-1}$ . The atmosphere was static air. Buoyancy correction was applied. The samples were taken in tall narrow crucibles to avoid loss by spattering.

### Treatment of data

The instrumental TG traces were redrawn as mass vs. temperature (TG), curves and also as the rate of loss of mass vs. temperature (DTG) curves. TG and DTG traces of the two chelates are presented in Fig. 1.

### Mathematical analysis of the TG curves

The curve for  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  complex exhibited a two stage decomposition pattern and that for  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$  complex exhibited a three stage

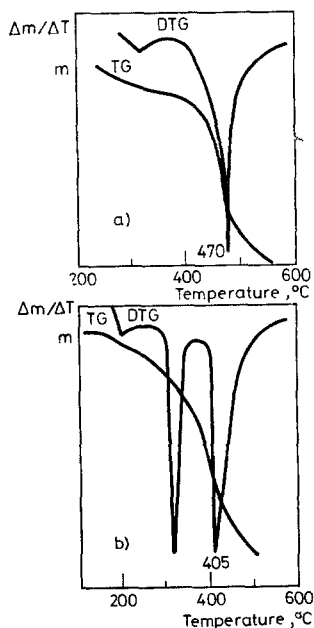


Fig. 1 TG and DTG curves of a =  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$ ; b =  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$

**Table 1** Thermal decomposition data

Substance	Peak temperature in DTG, °C	Temperature ranges in DTG, °C	Loss of mass, %			Probable assignment
			From TG	Theoretical	From independent pyrolysis	
[Th(FAN) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	320	200–400	11.28	12.07	—	Loss of 2 NO <sub>3</sub>
	470	420–500	72.25	74.29	73.5	Loss of 2 ligand molecules
	240	120–300	8.8	8.1	—	Loss of 4H <sub>2</sub> O molecules
[Th(CPAN) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	320	310–320	8.8	9.9	—	Loss of 2 CO <sub>2</sub>
	405	330–475	71.1	70.1	70.5	Loss of 2 ligand molecules

decomposition pattern. The last stage represents the major decomposition step in each case and mass loss considerations and X-ray diffraction data confirmed the product to be ThO<sub>2</sub>. The last stage was chosen for detailed study. For this purpose the relevant portion of the TG curves was redrawn on an expanded scale, using standard curve sets. Three different methods were used to evaluate kinetic data from these TG traces.

The differential method using Freeman–Carroll equation [15].

The Freeman–Carroll equation was used in the form

$$\frac{\Delta \log \frac{dw}{dt}}{\Delta \log w_y} = \frac{(-E^*/2.303 R)\Delta(T^{-1})}{\Delta \log w_y} + n \quad (1)$$

where  $w_y = w_\alpha - w$ ,  $w_\alpha$  = mass loss at the completion of the reaction,  $w$  = mass loss upto time  $t$ ,  $T$  = absolute temperature at time  $t$ ,  $n$  = order of reaction,  $R$  = gas constant in cal and  $E^*$  = energy of activation in J mol<sup>-1</sup>. Of the above terms,  $w_y$  and  $T$  can be directly obtained from the TG traces. The mass-temperature gradient ( $dw/dt$ ) could be obtained by drawing tangents. The temperature slopes,  $dw/dT$ , were converted into time slopes,  $dw/dt$ , using the relation,

$$dw/dt = (dw/dT) (dT/dt) = (dw/dT)\Phi \quad (2)$$

where  $\Phi$  is the heating rate. A plot of  $\frac{\Delta(T^{-1})}{\Delta \log w_y}$  versus  $\frac{\Delta \log (dw/dt)}{\Delta \log w_y}$  was drawn and found to be linear from which the order of reaction and activation energy were obtained from the intercept and slope respectively (Fig. 2). The order of reaction ( $n$ )

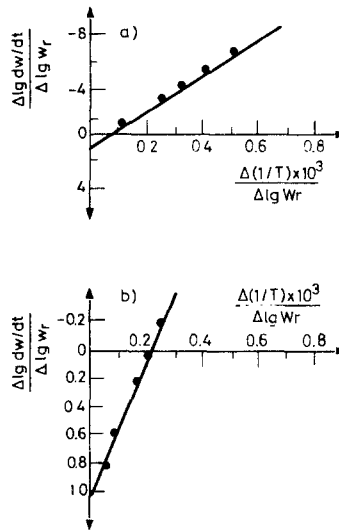


Fig. 2 Freeman-Carroll plots. a =  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$ ; b =  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$

was found to be almost unity. The usual first order rate law expression,

$$(dx/dt) = k(a-x) \quad (3)$$

can be put in the following form using the terms  $w$  and  $w_y$ .

$$(dw/dt) = kw_y \quad (4)$$

combining this with Arrhenius equation, i.e.,

$$k = Z \exp(-E^*/RT), \text{ we get} \quad (5)$$

$$\log [(dw/dt)/w_y] = \frac{-E^*}{2.303 RT} + \log Z \quad (6)$$

A plot of the left hand side expression against  $(T^{-1})$  was found to be linear, from the slope of which  $E^*$  was calculated.  $Z$  was calculated from the intercept and entropy of activation  $\Delta S^*$  was obtained from the equation,

$$Z = \frac{kT_s}{h} \exp(\Delta S^*/R) \quad (7)$$

where  $k$  is the Boltzman constant and  $h$  is the Planck's constant and  $T_s$  is the peak temperature from DTG. Typical curves concerning the application of the Freeman-Carroll equation ( $n=1$ ) to the two chelates are given in Fig. 3.

The integral method using the Coats-Redfern equation [16].

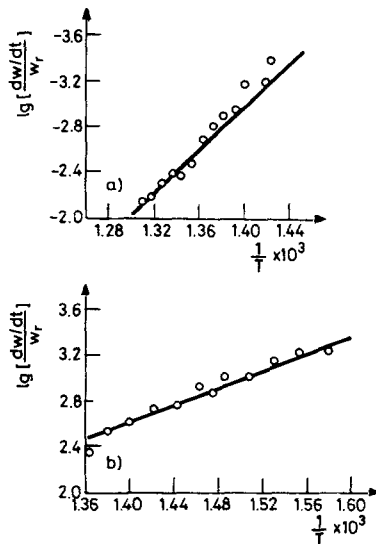


Fig. 3 Freeman-Carroll (modified) plots. a = [Th(FAN)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]; b = [Th(CPAN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O

Coats-Redfern equation, which is a typical integral method can be represented as

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = Z/\Phi \int_0^T \exp(-E^*/RT) dt \tag{8}$$

The left hand side of Eq. (8) has two different solutions, namely

$$1 - (1-\alpha)^{1-n}/(1-n) \text{ for } n \neq 1 \tag{9}$$

and

$$-\log(1-\alpha) \text{ for } n=1 \tag{10}$$

In both cases, the right hand side of Eq. (8) has the solution

$$ZRT^2/\Phi E^*(1-2RT/E^*) \exp(-E^*/RT) \tag{11}$$

Equations (12) and (13) are obtained after taking logarithms

$$\log [1 - (1-\alpha)^{1-n}/T^2(1-n)] =$$

$$\log ZR/\Phi E^*(1-2RT/E^*) - E^*/2.303 RT \text{ for } n \neq 1 \tag{12}$$

and

$$\log [-\log(1-\alpha)/T^2] = \log ZR/\Phi E^*(1-2RT/E^*) - E^*/2.303 RT \tag{13}$$

for  $n=1$

In ordinary thermal decomposition reactions,  $\log ZR/\Phi E^*(1-2RT/E^*)$  is

practically constant, and plots of

$$\log [1 - (1 - \alpha)^{1-n}/T^2(1-n)] \text{ vs. } 1/T \text{ for } n \neq 1 \quad (14)$$

and

$$\log [-\log (1 - \alpha)/T^2] \text{ vs. } 1/T \text{ for } n = 1 \quad (15)$$

respectively result in a straight line with a slope of  $E^*/2.303 R$  for the correctly chosen value of  $n$ . The reaction order can easily be estimated by observing the lines drawn by using  $n = 0.5$  and  $0.67$  in Eq. (14) and  $n = 1$  in Eq. (15). The application of Eqs (14) and (15) to our data on the Th(IV) chelates revealed that a better straight line results with Eq. (15) and, hence the order of the reaction is unity.

For a first order process the Coats–Redfern equation may be written in the form

$$\log \ln \frac{w_\alpha}{T^2} = \log \frac{[ZR(1-2RT)]}{\Phi E} - \frac{E^*}{2.303 RT} \quad (16)$$

Since  $1 - \frac{2RT}{E^*} \approx 1$ , a plot of L.H.S. against  $1/T$  was drawn (Fig. 4)  $E^*$  was calculated from the slope and  $Z$  was found out from the intercept.

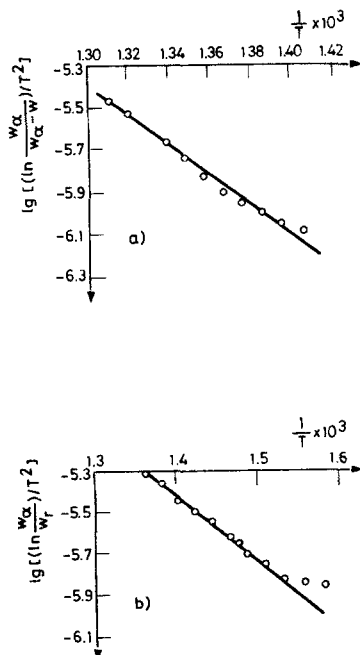


Fig. 4 Coats–Redfern plots. a =  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$ ; b =  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]_2\text{H}_2\text{O}$

The approximation method using the Horowitz–Metzger equation [17].

The Horowitz–Metzger method is illustrative of the approximation methods. These authors derive the relation

$$\log \frac{[1 - (1 - \alpha)^{1-n}]}{1-n} = \frac{E\Theta}{2.303 RT_s^2} \text{ for } n \neq 1 \quad (17)$$

when  $n = 1$ , the LHS of Eq. (17) would be  $\log(-\ln/1 - \alpha)$ . They have also derived a simple relation for obtaining the order of the reaction,  $n$ .

$$C_s = n^{1/(1-n)} \quad (18)$$

Where  $C_s = 1 - \alpha_s$  and  $\alpha_s$  is the fraction decomposed at the DTG peak temperature  $T_s$ . The application of master curve method [18] to our data on the Th(IV) chelates revealed that  $n$  is near to unity (Fig. 5).

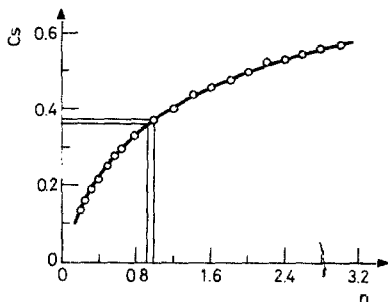


Fig. 5 Master curve: A:  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2] - C_s = 0.36$ ; B:  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O} - C_s = 0.375$

The Horowitz–Metzger equation applicable to first order kinetic process, is in the form

$$\log \log \frac{w_\alpha}{w_\gamma} = E^*\Theta/2.303 RT_s^2 - \log 2.303 \quad (19)$$

where  $\Theta = T - T_s$  and the other terms are as described earlier. A plot of  $\log [\log (w_\alpha/w_\gamma)]$  vs.  $\Theta$  was drawn and was found to be linear, from the slope of which  $E^*$  was calculated. Typical curves are given in Fig. 6. The preexponential factor  $Z$  was calculated from the equation

$$E^*/RT_s^2 = Z/\Phi \exp(-E^*/RT_s) \quad (20)$$

The entropy of activation  $\Delta S^*$  was calculated from the equation used earlier for the purpose.

Zsakó's modified Doyle method [19, 20].

The trial and error method of Doyle was modified by Zsakó by introducing the standard deviation instead of curve fitting method for the calculations.

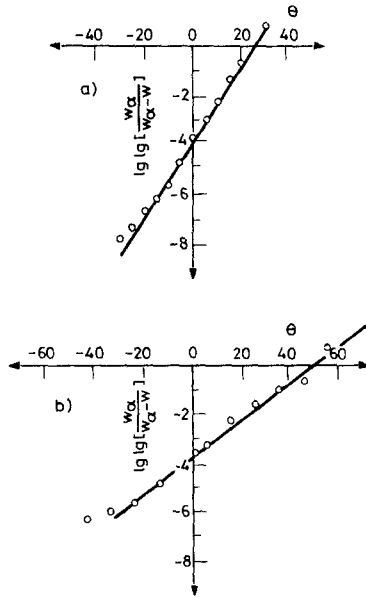


Fig. 6 Horowitz-Metzger plots: a:  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$ ; b:  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$

Th complex of CPAN was taken for this study. The value of  $g(\alpha)$  was calculated for various values of 'n' in the general equation  $\frac{d\alpha}{dt} = k(1-\alpha)^n$ , where 'n' can be considered as apparent reaction order. The values of 'n' taken are  $n=0, 0.5, 0.67, 1$  or 2.

If the logarithm of Doyle's equation is taken,

$$\log ZE^*/R\Phi = \log g(\alpha) - \log P(x) = B \quad (21)$$

where  $g(\alpha)$  is a certain function of  $\alpha$ , where  $\alpha$  stands for the fraction of initial compound reacted,  $Z$  = frequency factor,  $E^*$  = activation energy,  $R$  = gas constant,  $\Phi$  = heating rate. The values of the integral

$$P(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du \quad \left( \text{where } u = \frac{E^*}{RT} \right) \quad (22)$$

were calculated and tabulated by Doyle for  $x$  values covering a range from 10 to 50 and these values were used in calculating 'B'.

The  $-\log P(x)$  values were taken corresponding to over a range of 14 to 20  $E^*$  values (as  $E^*$  value according to graphical method is 15 kcal/mol and over a temperature range of 380 to 430 K).



The average of  $B$  values, as obtained at different values of  $E^*$  and at different temperatures, was taken and

$$\delta = \frac{(B_i - \bar{B})^2}{\gamma} \quad (23)$$

Where  $B_i$  is any value,  $\bar{B}$  is arithmetical mean  $\gamma$  is number of values.  $\delta$  values for various ' $B$ ' value are calculated similarly and given in Table 2.

**Table 2** Zsakó's modified method,  $\delta$  values

$EA$	$b=0$ $\delta$	$b=0.5$ $\delta$	$b=0.67$ $\delta$	$b=1$ $\delta$	$b=2$ $\delta$
14	0.004496	0.018165	0.009386	0.000653	0.004277
15	0.002684	0.014623	0.008716	0.000257	0.010359
16	0.00520	0.003224	0.008160	0.002102	0.017623
18	0.00758	0.004939	0.008775	0.005106	0.005792
20	—	0.018493	0.011674	0.004119	0.004847

\* The  $\delta$  value is minimum if the apparent order of reaction  $n$  is taken as, 1 i.e., 1st order reaction. Thus from tested ' $n$ ' values,  $n=1$  is the best.

## Results and discussion

The decomposition temperature ranges for the metal chelates are given in Table 1. Data from independent pyrolytic experiments are also included in this Table. Kinetic parameters calculated by employing the Freeman-Carroll, the Coats-Redfern and the Horowitz-Metzger equation are summarised in Table 3.

### Thermal behaviour

The DTG curve for  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  gives 2 peaks as may be seen from Table 1. The very strong DTG peak at  $470^\circ$  is a well-defined and non-overlapping one. Mass loss at the end of this stage, read from the TG curve, is 72.25%. X-ray diffraction study showed that the final product is  $\text{ThO}_2$ . The theoretical mass loss at this stage for the decomposition of  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  to  $\text{ThO}_2$  would be 74.29%, if we assume that the other decomposition products have completely volatilized off. Since the latter assumption is not completely correct, the discrepancy is justifiable.

In the case of  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  a three stage decomposition pattern is observed. The main decomposition stage is represented by a DTG peak at  $405^\circ$ . The overall loss of mass from the TG curve is 71.1% whilst the theoretical loss in mass

Table 3 Kinetic data

Substance	Parameters	From Freeman-Carroll equation	From Coats-Redfern equation	From Horowitz-Metzger equation	From Zsakó's modified Doyle method
[Th(FAN) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] <i>m</i> = 47.97 mg <i>w</i> <sub>2</sub> = 34.656 mg	<i>E</i> *, kJ mole <sup>-1</sup>	159.5	147	162	
	<i>Z</i> , s <sup>-1</sup>	6.79 × 10 <sup>8</sup>	7.09 × 10 <sup>7</sup>	9.47 × 10 <sup>8</sup>	
	Δ <i>S</i> *, J mole <sup>-1</sup> K <sup>-1</sup>	-83.4	-102.2	-80.7	
[Th(CPAN) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O <i>m</i> = 76.30 mg <i>w</i> <sub>2</sub> = 51.901 mg	<i>E</i> *, kJ mole <sup>-1</sup>	70.9	63.8	70	62.79
	<i>Z</i> , s <sup>-1</sup>	7.79 × 10 <sup>2</sup>	1.16 × 10 <sup>2</sup>	4.07 × 10 <sup>2</sup>	
	Δ <i>S</i> *, J mole <sup>-1</sup> K <sup>-1</sup>	-196.5	-212.3	-201.9	--

for the conversion  $\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O} \rightarrow \text{ThO}_2$  is 70.1%. The end product is confirmed to be  $\text{ThO}_2$  from its X-ray diffraction pattern.

In  $\text{Th}(\text{CPAN})_2\cdot 4\text{H}_2\text{O}$  complex,  $2\text{H}_2\text{O}$  molecules are lost below  $150^\circ$ . According to Nikolaev et al. [21] water eliminated below  $150^\circ$  can be considered as the water of crystallisation and water eliminated above  $150^\circ$  as coordinated water. So two of the water molecules present are water of crystallization. Initial decomposition temperature and inflection temperature have been used to determine the thermal stability of metal chelates. On the basis of the experimental findings in the present course of studies and observations made by earlier workers [22, 23] the relative thermal stabilities of the thorium chelates can be given as



#### *Decomposition kinetics*

In studying the decomposition kinetics, four methods mentioned in the literature were chosen, the Freeman–Carroll, the Coats–Redfern, the Horowitz–Metzger and the Zsakó's equations. In the case of the derivation method the most precise kinetic data are obtained when medium steep parts of the thermogravimetric curves are taken for computation. The analysis of data using the Freeman–Carroll equation gives a value of the order of the reaction  $n=0.90$  for the decomposition of  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  and  $n=1.02$  for that of  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ . The values of 'n' determined with the aid of Horowitz–Metzger's master curve are 0.95 and 1.0, respectively. The value of apparent reaction order calculated by Zsakó's modified Doyle method is  $n=1$  for  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ . The Coats–Redfern method seems to be more accurate but considerably time consuming.

**Table 4** X-ray powder diffraction data

Substance	d-spacing observed, Å	Intensity order (observed)	Sub- stance	d-spacing (ASTM date file) Å	Intensity grading from (ASTM data file)
Final product from $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$	3.232	1			
	1.688	2			
	1.980	3			
Final product from $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	3.231	1	$\text{ThO}_2$	3.234	100
	1.688	2		1.689	64
	1.981	3		1.980	58

The energy of activation obtained from the application of the Freeman–Carroll equation are for

$$\text{Th}[\text{FAN}]_2(\text{NO}_3)_2, E^* = 159.5 \text{ kJ/mole}^{-1}$$

for

$$[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}, E^* = 70.9 \text{ kJ/mole}^{-1}.$$

The Coats–Redfern equation gives the values for activation energy  $E^* = 147 \text{ kJ mole}^{-1}$  for the decomposition of  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  and  $E^* = 63.8 \text{ kJ mole}^{-1}$  for the decomposition of  $[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ . Somewhat similar values are obtained by the application of Horowitz–Metzger equation, they are:

$$\text{for } [\text{Th}(\text{FAN})_2(\text{NO}_3)_2] = 162.6 \text{ kJ mole}^{-1}$$

$$\text{for } [\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}, E^* = 70 \text{ kJ mole}^{-1}.$$

The entropies of activation vary from  $-81$  to  $-215 \text{ J mole}^{-1} \text{ K}^{-1}$ . The negative values indicate that the activated complexes have a more ordered structure than the reactants and that the reactions are ‘slower than normal’ [24].

$[\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$  decomposes at  $120^\circ$  since water present in the chelate gets eliminated at a lower temperature followed by decarboxylation of the coordinated ligand resulting in a low value for  $E^*$ . In the  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2]$  complex, the first step of decomposition is the elimination of  $2 \text{ NO}_3$  groups which starts only at  $200^\circ$  and therefore a higher value for  $E^*$  results.

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**Zusammenfassung** — Die thermische Zersetzung von Thorium(IV)-Chelaten von 1-(2-Fluorenylazo)-2-naphthol und *o*-Carboxyphenylazo-2-naphthol wurde thermogravimetrisch untersucht. Thermoanalytische Daten (TG und DTG) dieser Chelate werden angegeben und interpretiert. Reaktionsordnung sowie Aktivierungsenergie und -entropie wurden nach der differentiellen Methode unter Anwendung der Freeman-Carroll-Gleichung, nach der integralen Methode unter Verwendung der Coats-Redfern-Gleichung und nach der Näherungsmethode von Horowitz-Metzger bestimmt. Für die relative thermische Stabilität wird die Reihenfolge  $[\text{Th}(\text{FAN})_2(\text{NO}_3)_2] > [\text{Th}(\text{CPAN})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$  angegeben.

**Резюме** — Методом ТГ изучено термическое разложение хелатов четырехвалентного тория с 1-(2-флуоренилазо)-2-нафтолом и *o*-карбокисфенилазо-2-нафтолом, для которых представлены также данные ДТГ. Приведена интерпретация и математический анализ полученных данных, а также определен порядок реакции. Энергия активации и энтропия реакции были определены дифференциальным методом на основе уравнения Фримена-Кэрролла, интегральным методом, используя уравнение Коутса-Рэдферна и методом приближения на основе уравнения Хоровица-Метцгера. Установлена большая термоустойчивость первого хелата.