Journal of Thermal Analysis, Vol. 15 (1979) 3–10

KINETICS OF THERMAL DECOMPOSITION OF TRIVALENT METAL COMPLEXES WITH ALL-CIS-1,2,3,4-CYCLOPENTANE TETRACARBOXYLIC ACID

G. A. RAMA RAO and K. SRINIVASULU,

School of Studies in Chemistry, Vikram University, Ujjain — 456010 India

(Received May 18, 1977; in revised form February 22, 1978)

All-cis-1, 2, 3, 4-cyclopentane tetracarboxylic acid forms 1 : 1 complexes with metals like Al(III), Y(III) and Ga(III), and have been isolated in solid state from the aqueous solutions. Thermogravimetry of these complexes supports the probable formulae assigned on the basis of elemental analysis. Kinetics of some of the thermal decompositions have been studied. Various kinetic parameters such as apparent activation energy, order of decomposition, frequency factor and activation entropy have been evaluated and the former two constants have been compared by two methods and are in reasonable agreement with each other.

Experimental

A Cahn RG Electrobalance with a Rikedenki Kogyo Co., Ltd. recorder (Model B 140) operating on 1 mv full scale has been used to obtain the TG curve and a Honeywell Brown recorder used for the temperature vs time curves. For recording the sample temperature a chromel–alumel thermocouple was placed 3–4 mm below the sample holder which is a platinum boat 2 mm deep 8 mm diameter. A 6°/min heating rate has been employed in this work. The chart speed is maintained at 200 mm/hr.

Results and discussion

Freeman and Carroll [1] derived equation for a linear relationship between

$$\frac{\Delta(1/T)}{\Delta \log W_r} \text{ and } \frac{\Delta \log \frac{dw}{dt}}{\Delta \log W_r}$$

Where T = absolute temperature, $W_r = W_c - W$ and W_c = weight loss at completion of the reaction, W = total weight loss up to time t.

This results in a straight line with a slope equivalent to $E^*/2.3R$ and the intercept of $-x$ where E^* = energy of activation, x = order of decomposition process.

The validity of this graphical method has been supported by the Doyle method

[2] as modified by Zsakó [3] employing standard deviations in the calculations instead of curve fitting procedure.

Doyle's equation for TG curve is

$$g(\alpha) = \frac{ZE_a}{Rq} P(x) \tag{1}$$

Where $Z =$ frequency factor, $E_a =$ activation energy, $R =$ gas constant, $q =$ heating rate.
The value $g(\alpha)$ is a certain function of α, and

$$\alpha = \frac{W_0 - W}{W_0 - W_t} \tag{2}$$

Where W, W_0, W_t are the actual, initial and final weights of the sample respectively.

The value of $P(x)$ depends essentially both on temperature and activation energy.

The $g(\alpha)$ may be calculated for various values of 'b' (order of decomposition)

$$\frac{d\alpha}{dt} = K(1 - \alpha)^b \tag{3}$$

The values for b are considered as 0, 1 and 2.
When $b = 0$, $g_0(\alpha) = \alpha$

or
$$B_0 = \log g_0(\alpha) - \log P(x) \tag{4}$$
$$b = 1, g_1(\alpha) = - \ln(1 - \alpha)$$

or
$$B_1 = \log g_1(\alpha) - \log P(x) \tag{5}$$
$$b = 2, \ g_2(\alpha) = \frac{\alpha}{1 - \alpha}$$

or
$$B_2 = \log g_2(\alpha) - \log P(x) \tag{6}$$

The average of the 'B' values at different temperatures for the presumed order of reaction, say, at 0,1 and 2 have been calculated and their δ values have been determined employing the relation for standard deviation.

$$\delta = \sqrt{\frac{(B_i - \bar{B})^2}{r}} \tag{7}$$

Where B_i is any value, $\bar{B}$ is arithmetical mean, r is number of values.

The δ value at a particular temperature is minimum for a particular 'b' value (i.e.) the apparent reaction order. Using interpolated $-\log P(x)$ at each temperature, the δ values have been calculated for E_a values in a close range. The correct value for E_a gives minimum δ value at the particular 'b'.

The apparent frequency factor Z is calculated by the equation

$$\log Z = \bar{B} + \log Rq - \log E_a \tag{8}$$

and the apparent activation entropy as $S^* = 2.303 \log \frac{Zh}{KT}$ (9)

The value for T is taken as the temperature ($T\,1/2$) at which the weight loss is half of the total weight loss during the considered step.

Preparation of compounds

Equal volumes of equimolar (0.1M) solutions of metal and ligand were mixed in aqueous medium, the pH of the mixture was raised until complete precipitation had occurred. The determined pH ranges for complete precipitation are 4.75 – 5.00, 4.5 – 4.75, 4.25 – 4.5 for aluminium, yttrium and gallium, respectively. After precipitation, the salts were filtered, washed with water and dried at 100 °C. Metal contents were estimated by conventional gravimetric methods. Elemental analyses (carbon and hydrogen) were carried out and the probable formulae were assigned.

Al(CPTA) · $10H_2O$

Experimental : M = 6.02%, C = 24.63%, H = 5.29%
Calculated : M = 5.99%, C = 23.98%, H = 5.78%

Y(CPTA) · $7H_2O$

Experimental : M = 24.78%, C = 23.00%, H = 4.26%
Calculated : M = 24.64%, C = 23.56%, H = 4.37%

Ga(CPTA) · $10H_2O$

Experimental : M = 14.16%, C = 22.19%, H = 3.92%
Calculated : M = 14.14%, C = 21.91%, H = 5.28%

Aluminium complex

The probable formula Al L.$10H_2O$ assigned on the basis of elemental analysis has been well supported by the thermogravimetric studies (see Fig. 1). Here the decomposition is a continuous process, however, with two small sloping inflections at 120 ° where the loss of weight corresponds to the loss of 8 water molecules and the one at 370°, where the weight loss corresponds to 2 water molecules which might be expected to be present as co-ordinated water. The anhydrous complex starts decomposing at 380° and the process is completed at 540 ° leaving metal oxide as the end product.

Kinetic parameters have been calculated by two methods for the latter two major stages of decomposition. The activation energy and the reaction order have been calculated as 17.08 Kcal/mol and −0.4 respectively be Freeman and Carroll graphical method for the second stage of decomposition of co-ordinated water with the following data (Table 1).

The values of B calculated by the Zsakó method at different temperatures for the decomposition of co-ordinated water are listed in Table 2.

Table 1

$\frac{\Delta(T^{-1})}{\Delta \log W_r} \cdot 10^3\ K^{-1}$	$\frac{\Delta \log \frac{dW}{dt}}{\Delta \log W_r}$
2.55	11.00
1.61	5.42
1.59	4.52
1.42	4.15
1.02	2.71

Table 2

Sample weights and log $g(\alpha)$ data of hydrated Al−CPTA complex at different temperatures

Temperature, °C	W, mg	B_0 log α	B_1 log (ln 1/1−α)	B_2 log ' (α/1−α)
160	9 08	−0.7870	−0.7496	−0.7096
180	8.92	−0.6110	−0.5519	−0.4890
200	8.78	−0.4999	−0.4203	−0.3347
210	8.70	−0.4472	−0.3553	−0.2553
220	8.61	−0.3946	−0.2879	−0.1705
240	8.49	−0.3332	−0.2053	−0.1622
260	8.38	−0.2837	−0.1342	+0.0355
280	8.22	−0.2204	−0.0361	+0.1797
300	8.10	−0.1783	+0.0363	+0.2945
320	7.90	−0.1161	+0.1607	+0.5134

$W_0 = 9.4$ mg and $W_c = 7.48$ mg

Table 3

		δ	
E_a	$b = 0$	$b = 1$	$b = 2$
18	0.02302	—	—
16	0.01872	0.02025	0.05233
14	0.01543	0.01696	0.04904
12	0.01104	0.01257	0.04464
10	0.02182	0.02610	0.04728

The δ values for $b = 0$, 1 and 2 at different presumed activation energies are shown in Table 3.

The δ value is minimum if the order of reaction is taken as $b = 0$ i.e. the '0' order and hence the value of E_a is chosen as 12.0 Kcal/mol and this value corresponds to $\bar{B}_0 = 7.019$.

The frequency factor 'Z' has been calculated as $10.45 \cdot 10^6$. The apparent activation entropy has been calculated as -13.10 eu.

Kinetic parameters have been evaluated for the process of decomposition of the anhydrous complex. Activation energy and order of reaction have been obtained as 34.96 Kcal/mol and 0.2 respectively by the graphical method.

The δ value is minimum if the order of reaction is taken as $b = 1$ i.e. first order and the value of E_a is 34 Kcal/mol which corresponds to $\bar{B}_1 = 12.7163$.

The frequency factor 'Z' and the activation entropy have been calculated as $23.12 \cdot 10^{11}$ and -1.424 eu.

Yttrium complex

The analysis of the thermogravimetric curve supports the formula $YL.7H_2O$ assigned on the basis of elemental analysis (see Fig. 1). The water molecules are completely lost at 395° and the weight loss at the first inflection point at 200° would suggest the loss of 5 water molecules. The second stage significantly involves

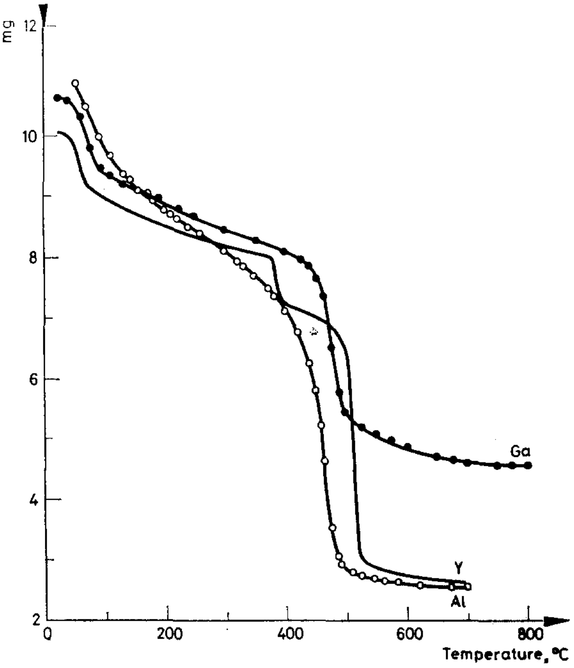

Fig. 1. TG curves for $AlL \cdot 10H_2O$, $YL \cdot 7H_2O$ and $GaL \cdot 10H_2O$

the decomposition of two co-ordinated water molecules up to 395° followed by the decomposition of anhydrous complex which is complete at 650° to leave the metal oxide as residue. Kinetic parameters have been calculated for the latter two major stages of decomposition.

The activation energy and order of reaction have been calculated for the second stage by the graphical method as 15.33 Kcal/mol and 1.6 respectively.

The δ values for $b = 0$, 1 and 2 suggest the reaction order as 2 at an activation energy of 14 Kcal/mol which corresponds to $\bar{B}_2 = 7.0032$.

The frequency factor 'Z' and entropy S^* have been calculated as $86.36 \cdot 10^5$ and -13.74 eu.

The activation energy and order of reaction have been obtained as 36.81 Kcal/mol and 1.2 by the graphical method for the decomposition curve of anhydrous complex.

The δ values indicate the order of reaction as 2 and the activation energy as 28 Kcal/mol which corresponds to $\bar{B}_2 = 9.8453$. The frequency factor Z and the entropy S^* have been calculated as $30.01 \cdot 10^8$ and -8.19 eu respectively.

Gallium complex

Calculations of the weight loss in the curve support the probable formula $GaL \cdot 10H_2O$ (see Fig. 1). The presence of two inflections at 115° and at 460° is indicated and the weights suggest the loss of 8 and 2 water molecules respectively at these temperatures and the latter might be co-ordinated water. The kinetic

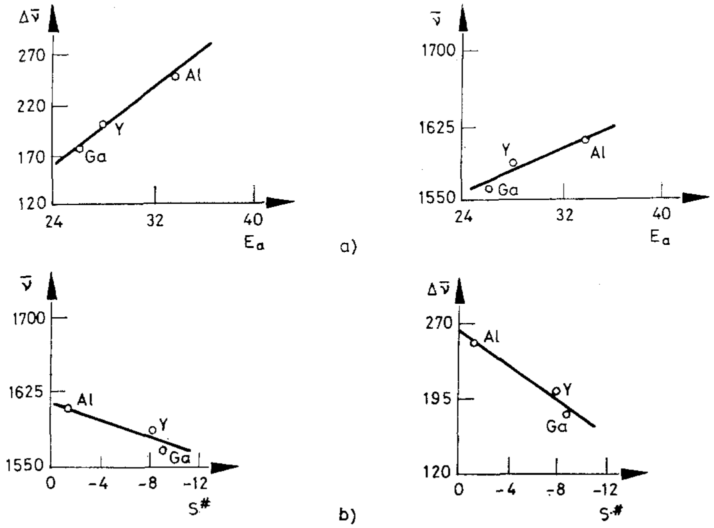

Fig. 2. Kinetic parameters in function of a) antisymmetric-, b) symmetric stretching frequencies of carboxyl groups

parameters have been evaluated for this process. The anhydrous complex starts decomposing at 460° and completes at 700° leaving metal oxide.

The values of $E_a = 16.57$ Kcal/mole and 0.4 as order of reaction have been obtained by employing the graphical method for the decomposition of co-ordinated water.

The δ values for $b = 0$, 1 and 2 suggest $b = 2$ and $E_a = 12$ Kcal/mol at $\bar{B}_2 = 7.5272$. Frequency factor Z and entropy S^* have been calculated as $33.21 \cdot 10^6$ and -11.93 eu respectively.

Order of reaction and activation energy for the decomposition process of anhydrous complex have been calculated by the graphical method as '0' and 26.55 Kcal/mol.

The δ value is minimum at $b = 0$ and $E_a = 26$ Kcal/mol and $\bar{B}_0 = 9.5984$. The frequency factor Z and activation entropy S^* have been calculated as $18.31 \cdot 10^8$ and -8.62 eu respectively.

Table 4

Kinetic parameters of CPTA complexes of Al(III), Y(III) and Ga(III) by two methods

		E_a, Kcal/mol	b	Z	S^*
Al	II	12 (17.08)	0 (−0.4)	$10.45 \cdot 10^6$	−13.10
	III	34 (34.96)	1 (0.2)	$23.12 \cdot 10^{11}$	− 1.42
Y	II	14 (15.33)	2 (1.6)	$86.36 \cdot 10^5$	−13.74
	III	28 (36.81)	2 (1.2)	$30.01 \cdot 10^8$	− 8.194
Ga	II	12 (16.57)	2 (0.4)	$33.21 \cdot 10^6$	−11.93
	III	26 (26.55)	0 (0)	$18.31 \cdot 10^8$	−8.618

The values in the brackets are of the Freeman-Carroll method

Conclusion

The data presented in this study may aid the understanding of the reaction mechanism in solid state. These kinetic parameters have significant bearing in exhibiting a linear relationship with carboxyl antisymmetric ($\bar{\nu}$) stretching frequencies from IR studies. The difference in the antisymmetric and symmetric stretching frequencies ($\Delta\bar{\nu}$) also shows a similar relationship with these constants for the metals of the same oxidation state (see Figure 2).

*

The authors are thankful to the CSIR for the award of Research Fellowship to one of them (G. R. R.).

References

1. E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
2. C. D. Doyle, J. Appl. Polymer. Sci., 15 (1961) 285.
3. J. Zsakó, J. Phys. Chem., 72 (1968) 2406.

Résumé — L'acide all-cis-1,2,3,4-cyclopentanetétracarboxylique forme des complexes 1 : 1 avec les métaux tels que Al(III), Y(III) et Ga(III) et a été isolé à l'état solide à partir des solutions aqueuses. La thermogravimétrie de ces complexes vient à l'appui des formules probables établies par l'analyse élémentaire. La cinétique de la décomposition thermique de plusieurs d'entre eux a été étudiée. Divers paramètres cinétiques comme l'énergie d'activation, l'ordre de la décomposition, le facteur de fréquence et l'entropie d'activation ont été évalués. La comparaison des deux premières constantes obtenues par deux méthodes différentes montre une très bonne concordance des valeurs.

Zusammenfassung — All-cis-1,2,3,4-Cyclopentantetracarbonsäure bildet 1 : 1 Komplexe mit Metallen wie Al(III), Y(III) und Ga(III). Sie wurden in festem Zustand aus den wässerigen Lösungen isoliert. Die Thermogravimetrie dieser Komplexe unterstützt die wahrscheinlichen Formeln, welche den Verbindungen auf Grund der Elementaranalyse Zugeschrieben worden sind. Die Kinetik einiger dieser thermischen Zersetzungen wurde untersucht. Verschiedene kinetische Parameter, wie die scheinbare Aktivierungsenergie, die Ordnung der Zersetzung, der Frequenzfaktor und die Aktivierungsentropie wurden bewertet und die ersten beiden Konstanten mittels zweier Methoden verglichen und in guter Übereinstimmung mit einander gefunden.

Резюме — Алло-цис-1,2,3,4-циклопентантетракарбоновая кислота образует с Al(III), У(III) и Ga(III) комплексы состава 1 : 1, которые и были выделены в твердом состоянии из водных растворов. Термогравиметрия этих комплексов подтверждает возможную формулу их состава, установленную на основе элементарного анализа. Была изучена кинетика некоторых термических распадов. Различные кинетические параметры, как например, кажущаяся энергия активации, порядок разложения, частотный фактор и активационная энтропия были вычислены, а первые две константы были сравнены двумя методами и хорошо согласовывались друг с другом.