Thermochimica Acta, 89 (1985) 295–305
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF SIMULTANEOUS VARIATION OF SAMPLE MASS AND HEATING RATE ON THE MECHANISM OF DEHYDRATION OF ZINC OXALATE DIHYDRATE

K. KRISHNAN and K.N. NINAN
Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Trivandrum 695022 (India)

P.M. MADHUSUDANAN
Sanskrit College, Pattambi, Kerala (India)

(Received 16 January 1985)

ABSTRACT

The mechanism of the single-step dehydration of $ZnC_2O_4 \cdot 2H_2O$ has been established from TG, DTA and DSC studies. The rate-controlling process for the reaction is random nucleation with the formation of one nucleus on each particle. The kinetic parameters are calculated from mechanistic as well as non-mechanistic kinetic equations. For the dehydration reaction, the activation energy and the pre-exponential factor show a systematic decrease with the simultaneous increase in sample mass and heating rate, whereas the mechanism of the process remains unaffected by these variations.

INTRODUCTION

In earlier publications [1,2], we evaluated the activation energy, E, pre-exponential factor, A, and order parameter, n, for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from TG, DTA and DSC studies. The effect of the simultaneous variation of sample mass and heating rate on these kinetic parameters was studied and multiparameter equations, which relate the temperature of inception of reaction, T_i, sample mass, m, heating rate, ϕ, sample temperature, T_α, at which a constant fraction, α, has decomposed, and activation energy, E, were derived.

Non-isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids [3–8], particularly dehydration reactions [9–11]. This study, therefore, attempts to establish the mechanism of the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from TG, DTA and DSC experiments. Similar studies by the TG method were carried out by earlier workers [9] for the thermal decomposition of $CaC_2O_4 \cdot H_2O$.

EXPERIMENTAL

Zinc oxalate dihydrate of 99.9% purity was used. The experiments were carried out using a DuPont 990 thermal analyser system in conjunction with a 951 TGA and cell base module II with 1200°C DTA and 902 DSC.

Six sets of sample mass (4, 6, 8, 10, 12 and 14 mg) and six heating rates (1, 2, 5, 10, 20 and 50°C $\min^{-1}$) were employed to study the effect of the simultaneous variations of sample mass and heating rate on the TG, DTA and DSC results. Further experimental details are given in our earlier publications [1,2]. The fractional decomposition, α, was determined directly from TG curves, whereas a numerical integration technique was used for DTA and DSC [2]. Calculations were done with a CDC computer using the FORTRAN IV program.

MATHEMATICAL ANALYSIS OF DATA

Evaluation of the mechanism of reactions from non-isothermal methods has been discussed by Šesták and Berggren [12] and Satava [13]. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\,\mathrm{e}^{-E/RT}\mathrm{f}(\alpha) \tag{1}$$

where A is the pre-exponential factor, t is the time and $\mathrm{f}(\alpha)$ depends on the mechanism of the process. For a linear heating rate, ϕ, $\mathrm{d}T/\mathrm{d}t = \phi$ and substitution into eqn. (1) gives

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{\phi}\mathrm{e}^{-E/RT}\mathrm{d}T \tag{2}$$

Integration of the left-hand side of eqn. (2) gives

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \mathrm{g}(\alpha) = \int_0^{T} \frac{A}{\phi}\mathrm{e}^{-E/RT}\mathrm{d}T \tag{3}$$

where $\mathrm{g}(\alpha)$ is the integrated form of $\mathrm{f}(\alpha)$. A series of $\mathrm{f}(\alpha)$ forms are proposed and the mechanism is obtained from that which gives the best representation of the experimental data. Nine probable reaction mechanisms given by Satava [13] are given in Table 1. For evaluating kinetic parameters from the mechanistic equations, the right-hand side of eqn. (3), the temperature integral, which is an incomplete gamma function, was used in the form given by Coats and Redfern [14], which is one of the best solutions, recommended by several authors [15–17].

TABLE 1

Commonly used g(α) forms for solid-state reactions

Eqn. No.	Form of g(α)	Rate-controlling process
1	α^2	One-dimensional diffusion
2	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two-dimensional diffusion
3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry, Jander equation
4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry, Ginstling–Brounshtein equation
5	$-\ln(1-\alpha)$	Random nucleation, one nucleus on each particle, Mampel equation
6	$[-\ln(1-\alpha)]^{1/2}$	Random nucleation, Avrami equation I
7	$[-\ln(1-\alpha)]^{1/3}$	Random nucleation, Avrami equation II
8	$1-(1-\alpha)^{1/2}$	Phase boundary reaction, cylindrical symmetry
9	$1-(1-\alpha)^{1/3}$	Phase boundary reaction, spherical symmetry

The general form of the equation used is

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{\phi E}-\frac{E}{RT} \qquad (4)$$

Along with the mechanistic equations, three non-mechanistic methods suggested by Coats and Redfern [14], MacCallum and Tanner [18] and Horowitz and Metzger [19] were also used for comparison. The order parameter, n, was determined by an iteration method described earlier [1].

Using the computer, linear plots were drawn for the nine forms of $\ln g(\alpha)/T^2$ versus $1/T$ by the method of least squares, and also for the appropriate linear forms of Coats–Redfern, MacCallum–Tanner and Horowitz–Metzger equations. E, A and the corresponding correlation coefficients, r, for the linear plots were calculated.

RESULTS AND DISCUSSION

The values of the temperature of inception of reaction (T_i) of the dehydration reaction are given in Table 2. The kinetic parameters calculated from TG, DTA and DSC for the nine mechanistic equations are given in Tables 3, 4 and 5, respectively. The corresponding values of E, A and r from non-mechanistic equations (Coats–Redfern, MacCallum–Tanner and Horowitz–Metzger) are given in Tables 6, 7 and 8, respectively.

From Tables 3–5, it can be seen that, irrespective of the thermal methods

TABLE 2

Variation of temperature of inception of reaction, T_i, with sample mass and heating rate in TG, DTA and DSC

Sample mass (mg)	Heating rate (°C min^{-1})	T_i (K)		
		TG	DTA	DSC
4	1	360	368	364
6	2	364	372	367
8	5	368	378	371
10	10	373	384	375
12	20	378	391	380
14	50	383	405	387

employed, the highest value of the correlation coefficient and, hence, the best-fit curve is obtained for the Mampel equation (eqn. 5) in the case of all six sets of experiments. We can thus infer that the rate-controlling process for the reaction is random nucleation with the formation of one nucleus on each particle. It can also be seen from these tables that some other equations give good linear curves with high values of correlation coefficients, so that it may become difficult to assign the reaction mechanisms unequivocally from the linearity of the kinetic curves alone. In such cases, some authors have chosen the function $g(\alpha)$, which gives kinetic parameters in agreement with those obtained by the numerical method proposed in ref. 20. In the present case, it is observed that for all the thermal methods employed, the E and A values obtained from the Coats–Redfern method with $n = 1$ are in good agreement with the E and A values from the Mampel equation, which is based on random nucleation.

The MacCallum–Tanner equation also gives E and A values which are in close agreement with those given by mechanistic and Coats–Redfern equations, whereas the Horowitz–Metzger equation gives higher values. The higher value is due to the inherent error involved in the approximation method employed in the derivation of the Horowitz–Metzger equation. From Tables 6–8, it can also be seen that the values of E and log A (obtained from mechanistic as well as non-mechanistic kinetic equations) are linearly related, which is due to the kinetic compensation effect [21].

It can be concluded that the mechanism of dehydration of $ZnC_2O_4 \cdot 2H_2O$ follows random nucleation with one nucleus on each particle and is independent of the thermal techniques used. The kinetic parameters obtained from the mechanistic equation show a systematic decrease with the simultaneous increase in sample mass and heating rate. However, it is seen that the mechanism of the dehydration reaction is not affected by the variations in sample mass and heating rate. The kinetic parameters obtained from TG experiments are lower than those from DTA and DSC values. This is in

TABLE 3

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from TG using mechanistic equations

Sample mass (mg)	Heating rate (°C min^{-1})	Parameter [a]	Mechanistic equation No.								
			1	2	3	4	5	6	7	8	9
4	1	E	88.48	96.42	106.6	99.77	58.62	28.30	18.35	50.03	52.55
		A	2.10×10^{46}	3.73×10^{50}	6.04×10^{55}	6.91×10^{51}	3.43×10^{30}	1.31×10^{7}	2.83×10^{7}	8.21×10^{24}	1.53×10^{26}
		r	0.9989	0.9867	0.9935	0.9894	0.9990	0.9966	0.9964	0.9904	0.9933
6	2	E	60.03	66.19	74.20	68.82	41.43	19.58	12.54	34.28	36.33
		A	4.93×10^{30}	1.01×10^{34}	1.03×10^{33}	7.61×10^{34}	1.32×10^{20}	1.73×10^{8}	1.43×10^{4}	1.79×10^{16}	1.72×10^{17}
		r	0.9844	0.9914	0.9970	0.9929	0.9991	0.9989	0.9988	0.9949	0.9968
8	5	E	46.49	50.69	56.05	52.45	29.70	14.29	8.990	25.92	27.24
		A	3.06×10^{22}	3.99×10^{24}	1.06×10^{27}	9.01×10^{24}	1.70×10^{13}	1.76×10^{5}	1.77×10^{2}	1.89×10^{11}	7.38×10^{11}
		r	0.9884	0.9938	0.9980	0.9955	0.9990	0.9988	0.9988	0.9962	0.9978
10	10	E	39.28	43.06	48.10	44.67	25.40	12.12	7.545	21.96	23.18
		A	1.18×10^{18}	7.91×10^{19}	1.01×10^{22}	1.41×10^{20}	5.18×10^{10}	1.18×10^{4}	3.48×10^{1}	8.89×10^{8}	2.94×10^{9}
		r	0.9847	0.9919	0.9975	0.9943	0.9990	0.9988	0.9986	0.9950	0.9973
12	20	E	29.62	32.78	36.96	34.15	21.08	9.100	5.492	16.59	17.62
		A	2.69×10^{12}	7.13×10^{13}	2.94×10^{15}	8.74×10^{13}	1.48×10^{8}	2.68×10^{2}	3.282	7.54×10^{5}	1.86×10^{6}
		r	0.9785	0.9875	0.9953	0.9907	0.9990	0.9983	0.9978	0.9913	0.9946
14	50	E	24.11	26.50	29.59	27.52	18.12	6.890	4.013	13.14	13.89
		A	2.42×10^{9}	2.30×10^{10}	2.22×10^{11}	1.76×10^{10}	1.19×10^{6}	2.72×10^{1}	9.690	1.29×10^{4}	2.23×10^{4}
		r	0.9793	0.9838	0.9926	0.9875	0.9986	0.9961	0.9944	0.9948	0.9914

[a] E in kcal mol; A in s^{-1}.

TABLE 4

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from DTA using mechanistic equations

Sample mass (mg)	Heating rate (°C min^{-1})	Parameter [a]	Mechanistic equation No.								
			1	2	3	4	5	6	7	8	9
4	1	E	125.4	136.4	151.9	141.7	96.40	41.21	26.90	71.43	75.26
		A	3.96×10^{68}	1.51×10^{74}	–	2.89×10^{77}	3.99×10^{52}	6.00×10^{20}	4.11×10^{12}	3.88×10^{37}	1.11×10^{39}
		r	0.9772	0.9853	0.9929	0.9969	0.9981	0.9967	0.9965	0.9896	0.9828
6	2	E	105.1	114.8	127.1	118.9	75.01	33.91	22.09	52.02	62.75
		A	3.21×10^{54}	3.58×10^{59}	5.54×10^{65}	1.40×10^{61}	4.33×10^{38}	8.10×10^{15}	2.14×10^{9}	4.81×10^{29}	1.59×10^{31}
		r	0.9786	0.9861	0.9931	0.9888	0.9980	0.9967	0.9966	0.9899	0.9929
8	5	E	67.87	74.38	82.82	77.21	48.80	21.84	14.09	38.56	40.63
		A	4.61×10^{34}	1.22×10^{38}	1.73×10^{42}	1.02×10^{39}	4.19×10^{23}	4.52×10^{9}	4.74×10^{5}	3.48×10^{18}	3.64×10^{19}
		r	0.9863	0.9924	0.9944	0.9987	0.9987	0.9988	0.9982	0.9952	0.9951
10	10	E	59.04	64.37	71.42	66.65	40.60	18.49	11.83	33.18	34.82
		A	1.34×10^{29}	5.92×10^{31}	9.08×10^{34}	2.38×10^{32}	1.95×10^{18}	5.38×10^{7}	1.07×10^{4}	1.77×10^{15}	1.00×10^{16}
		r	0.9844	0.9909	0.9964	0.9932	0.9989	0.9980	0.9980	0.9938	0.9962
12	20	E	43.52	47.35	52.26	48.91	32.46	13.87	9.001	24.15	25.38
		A	4.28×10^{20}	3.00×10^{22}	3.67×10^{24}	5.28×10^{22}	2.64×10^{13}	8.97×10^{4}	1.75×10^{2}	2.55×10^{10}	5.82×10^{14}
		r	0.9892	0.9944	0.9954	0.9961	0.9989	0.9984	0.9983	0.9967	0.9980
14	50	E	36.95	39.75	43.59	41.01	27.68	10.69	6.895	19.95	20.91
		A	6.17×10^{15}	1.33×10^{17}	3.09×10^{18}	1.37×10^{17}	2.37×10^{10}	2.65×10^{3}	2.052	4.71×10^{7}	1.00×10^{8}
		r	0.9852	0.9910	0.9961	0.9930	0.9981	0.9974	0.9975	0.9933	0.9957

[a] E in kcal mol^{-1}; A in s^{-1}.

TABLE 5

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from DSC using mechanistic equations

Sample mass (mg)	Heating rate (°C min^{-1})	Parameter [a]	Mechanistic equation No.								
			1	2	3	4	5	6	7	8	9
4	1	*E*	116.4	126.8	139.4	130.9	86.78	37.13	24.27	65.88	68.97
		A	1.52×10^{66}	8.47×10^{71}	–	5.85×10^{73}	1.02×10^{49}	1.66×10^{19}	2.98×10^{11}	9.15×10^{35}	4.56×10^{37}
		r	0.9783	0.9854	0.9921	0.9880	0.9982	0.9960	0.9958	0.9820	0.9920
6	2	*E*	93.21	100.6	109.9	103.7	64.93	28.74	18.77	51.91	54.18
		A	7.42×10^{50}	9.65×10^{54}	6.75×10^{59}	1.37×10^{56}	1.52×10^{35}	1.03×10^{14}	1.15×10^{14}	1.10×10^{27}	1.66×10^{28}
		r	0.9815	0.9879	0.9935	0.9900	0.9983	0.9967	0.9965	0.9908	0.9933
8	5	*E*	63.16	68.79	76.10	71.18	40.32	19.87	12.73	35.48	37.28
		A	5.11×10^{32}	4.97×10^{35}	2.01×10^{39}	2.74×10^{36}	1.35×10^{20}	5.75×10^{8}	4.33×10^{4}	1.58×10^{17}	8.11×10^{18}
		r	0.9841	0.9907	0.9964	0.9930	0.9986	0.9982	0.9983	0.9938	0.9965
10	10	*E*	54.12	58.63	64.31	60.49	34.46	16.43	10.43	29.96	31.36
		A	1.09×10^{27}	2.07×10^{29}	8.13×10^{31}	5.37×10^{29}	2.97×10^{16}	5.72×10^{6}	2.43×10^{3}	7.22×10^{13}	3.01×10^{14}
		r	0.9891	0.9941	0.9975	0.9957	0.9994	0.9984	0.9981	0.9964	0.9975
12	20	*E*	41.75	44.05	51.25	46.56	27.57	13.17	8.326	23.05	24.18
		A	2.29×10^{18}	2.52×10^{20}	6.71×10^{22}	5.68×10^{20}	6.77×10^{11}	3.79×10^{4}	9.38×10^{1}	1.57×10^{9}	2.02×10^{12}
		r	0.9725	0.9822	0.9915	0.9961	0.9994	0.9955	0.9950	0.9969	0.9909
14	50	*E*	32.89	36.30	40.78	37.77	24.69	10.03	6.225	18.36	19.46
		A	2.12×10^{13}	5.82×10^{14}	2.38×10^{11}	7.14×10^{14}	1.94×10^{9}	5.80×10^{2}	7.46	3.32×10^{5}	8.19×10^{6}
		r	0.9615	0.9731	0.9848	0.9975	0.9996	0.9900	0.9877	0.9975	0.9932

[a] *E* in kcal mol^{-1}; *A* in s^{-1}.

TABLE 6

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from TG, using mechanistic and non-mechanistic equations (E in kcal mol^{-1}; A in s^{-1})

Sample mass (mg)	Heating rate (°C min^{-1})	Mampel			Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
		E	A	r	E	A	r	E	A	r	E	A	r
4	1	58.62	3.43×10^{30}	0.9990	58.62	3.43×10^{30}	0.9990	58.65	6.85×10^{30}	0.9991	61.40	4.69×10^{31}	0.9988
6	2	41.43	1.31×10^{20}	0.9991	41.43	1.31×10^{20}	0.9991	42.20	2.55×10^{21}	0.9991	43.80	1.10×10^{22}	0.9988
8	5	29.70	1.70×10^{13}	0.9990	29.70	1.70×10^{13}	0.9990	30.61	1.07×10^{14}	0.9991	32.50	4.25×10^{15}	0.9987
10	10	25.40	5.18×10^{10}	0.9990	25.40	5.18×10^{10}	0.9990	26.95	5.58×10^{11}	0.9992	28.50	1.30×10^{13}	0.9987
12	20	21.08	1.48×10^{8}	0.9990	21.08	1.48×10^{8}	0.9990	21.95	1.14×10^{9}	0.9990	23.50	4.89×10^{9}	0.9982
14	50	18.12	1.19×10^{6}	0.9987	18.12	1.19×10^{6}	0.9987	19.10	3.28×10^{7}	0.9990	20.95	1.72×10^{8}	0.9982

TABLE 7

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from DTA, using mechanistic and non-mechanistic equations (E in kcal mol^{-1}; A in s^{-1})

Sample mass (mg)	Heating rate (°C min^{-1})	Mampel			Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
		E	A	r	E	A	r	E	A	r	E	A	r
4	1	96.40	3.99×10^{52}	0.9979	96.40	3.99×10^{52}	0.9979	96.21	6.44×10^{52}	0.9980	98.85	5.82×10^{54}	0.9965
6	2	75.01	4.33×10^{38}	0.9980	75.01	4.33×10^{38}	0.9980	74.89	5.60×10^{38}	0.9980	77.95	1.35×10^{40}	0.9975
8	5	48.80	4.19×10^{23}	0.9987	48.80	4.19×10^{23}	0.9987	48.67	9.04×10^{23}	0.9988	52.30	7.88×10^{24}	0.9980
10	10	40.60	1.95×10^{18}	0.9989	40.60	1.95×10^{18}	0.9989	40.61	3.06×10^{18}	0.9990	44.38	3.48×10^{20}	0.9981
12	20	32.46	2.64×10^{13}	0.9989	32.46	2.64×10^{13}	0.9989	32.40	5.42×10^{13}	0.9990	35.12	5.82×10^{14}	0.9979
14	50	27.68	2.37×10^{10}	0.9981	27.68	2.37×10^{10}	0.9981	27.60	3.01×10^{10}	0.9985	30.96	1.40×10^{11}	0.9975

TABLE 8

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from DSC, using mechanistic and non-mechanistic equations (E in kcal mol^{-1}; A in s^{-1})

Sample mass (mg)	Heating rate (°C min^{-1})	Mampel			Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
		E	A	r	E	A	r	E	A	r	E	A	r
4	1	86.78	1.02×10^{49}	0.9982	86.78	1.02×10^{49}	0.9982	86.75	1.76×10^{49}	0.9980	89.67	8.69×10^{51}	0.9975
6	2	64.93	1.52×10^{35}	0.9983	64.93	1.52×10^{35}	0.9983	64.86	3.68×10^{35}	0.9980	68.11	3.98×10^{37}	0.9976
8	5	40.32	1.35×10^{20}	0.9986	40.32	1.35×10^{20}	0.9986	40.15	3.62×10^{20}	0.9988	43.66	5.85×10^{22}	0.9981
10	10	34.46	2.97×10^{16}	0.9989	34.46	2.97×10^{16}	0.9989	34.23	3.70×10^{16}	0.9989	38.21	6.33×10^{18}	0.9985
12	20	27.57	6.77×10^{11}	0.9994	27.57	6.77×10^{11}	0.9994	27.37	7.87×10^{11}	0.9994	31.57	5.82×10^{13}	0.9989
14	50	24.69	1.94×10^{9}	0.9996	24.69	1.94×10^{9}	0.9996	23.86	3.01×10^{9}	0.9996	27.97	1.40×10^{11}	0.9985

agreement with our earlier observations [22]. In general, the values obtained from TG are more accurate due to the greater accuracy in the measurement of the mass. DTA and DSC give closer values since the inherent errors are comparable in both cases [23].

ACKNOWLEDGEMENTS

Two of us (KK and KNN) thank Mr. M.R. Kurup and Dr. K.V.C. Rao for their keen interest and encouragement.

REFERENCES

1 P.M. Madhusudanan, K. Krishnan and K.N. Ninan, Thermal Analysis, Vol. 1, Proc. 7th ICTA, Kingston, Ont., 1982, Wiley, New York, 1982, p. 226.
2 K. Krishnan, K.N. Ninan and P.M. Madhusudanan, Thermochim. Acta, 71 (1983) 305.
3 F. Skavara and V. Satava, J. Therm. Anal., 2 (1970) 325.
4 B. Carrol and E.P. Manche, Thermochim. Acta, 3 (1972) 449.
5 J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
6 W.W. Wendlandt, Thermal Methods of Analysis, 2nd edn., Wiley, New York, 1974.
7 C.G.R. Nair and P.M. Madhusudanan, Thermochim. Acta, 14 (1976) 373.
8 K.N. Ninan and C.G.R. Nair, Thermochim. Acta, 23 (1978) 161.
9 K.N. Ninan and C.G.R. Nair, Thermochim. Acta, 30 (1979) 25.
10 V. Satava and J. Šesták, Anal. Chem., 45 (1973) 154.
11 R. Giovanoli and R. Brutrseh, Thermochim. Acta, 13 (1975) 15.
12 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
13 V. Satava, Thermochim. Acta, 2 (1971) 2.
14 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
15 M.D. Juddo and M.T. Pope, J. Therm. Anal., 4 (1972) 31.
16 J. Zsako, J. Therm. Anal., 5 (1973) 239.
17 V.M. Gorbachev, J. Therm. Anal., 8 (1975) 349.
18 J.R. MacCallum and J. Tanner, Eur. Polym. J., 6 (1970) 1033.
19 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
20 P.H. Fong and D.T. Chen, Thermochim. Acta, 18 (1977) 273.
21 P.D. Garn, J. Therm. Anal., 10 (1976) 99.
22 P.M. Madhusudanan, K. Krishnan and K.N. Ninan, Proc. 3rd National Symposium on Thermal Analysis, Trivandrum, India, 1982, p. 46.
23 E.F. Palermo and J. Chiu, Thermochim. Acta, 14 (1976) 1.