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Thermochemical study of methabenzthiazuron

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Abstract

A calorimetric study of methabenzthiazuron (MBT) has provided evidence of chemical transformation in the solid state at room temperature. Traces of water vapour were absorbed to form a hydrate, which produces a binary eutectic system with MBT at a temperature of 380.3 K and an estimated mole fraction of MBT of $x_{\mathrm{A}} = 0.78$. The mean value of the hydration rate of MBT at room temperature is $\bar{V}_{\mathrm{A} \to \mathrm{B}} = 3.7 \times 10^{-5}$ mol% min^{-1}. The mean value of the thermal decomposition rate of MBT at the melting temperature $T^{\circ}_{\mathrm{m}} = 393.5$ K is $\bar{V}_{\mathrm{A}} = 0.01\%$ mol min^{-1}. The highest rate of decomposition, $\bar{V}_{\mathrm{E}} = 0.14\%$ mol min^{-1}, was observed at the eutectic temperature.

Keywords: Hydration; Phase transition; Stability

1. Introduction

Methabenzthiazuron (MBT) or [*N*-(2-benzthiazolyl)-*N*,*N*′-dimethylurea] is an active ingredient of herbicide, which controls weeds in cereal crops. Its effectiveness persists in the field soil for more than one growing season. For this reason the degradation of MBT in the soil was examined. *N*-Dimethylation has been commonly postulated as the initial step in the degradation of many substituted urea compounds. Point et al. [1] reported that MBT is transformed to a hydroxylmethyl derivative before it is dimethylated or conjugated with plant constituents. Dimethylation of the 3-methyl group of MBT by fungi was reported by Walnöfer et al. [2] and of the 1-methyl group in the soil was confirmed by Mittelstaedt and co-workers [3,4]. Dimethylation at the 3 position proceeds faster than at the 1 position, which

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indicates that benzthiazuron [*N*-(2-benzthiazolyl)-*N*′-methylurea] would be formed during the degradation. The possible products of degradation are *N*-(2-benzthiazolyl)urea, methylaminobenzthiazole, *N*-(2-benzthiazolyl)methylamine, benzthiazolylamine and benzthiazolone. Both *N*-(2-benzthiazolyl)methylamine and benzthiazolone degrade more rapidly than MBT [5]. However, little is known about the nature of the thermal degradation of high purity MBT.

The aim of this paper is to study the chemical and phase transitions of pure MBT using several DSC methods.

2. Experimental

All the samples of MBT were synthesized and purified in the Department of Analytical Chemistry at the Institute of Organic Industrial Chemistry, Warsaw. Samples I and III were synthesized and purified separately and over different periods of time. Sample II was obtained by additional crystallization of sample I from methanol, benzene and chloroform. All the samples had a purity, determined by GC or HPLC, of at least 99.9%, and were stored in plastic-capped bottles.

Measurements were performed on the heat-flux DSC 605 M UNIPAN calorimeter coupled with an IBM AT computer. The authors' own controlled analysis

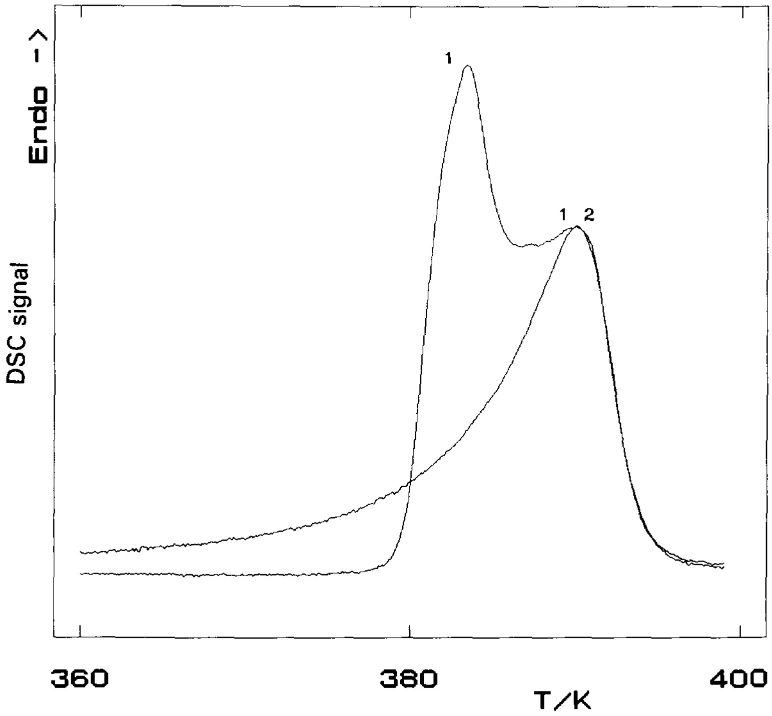

Fig. 1(A)

(B)

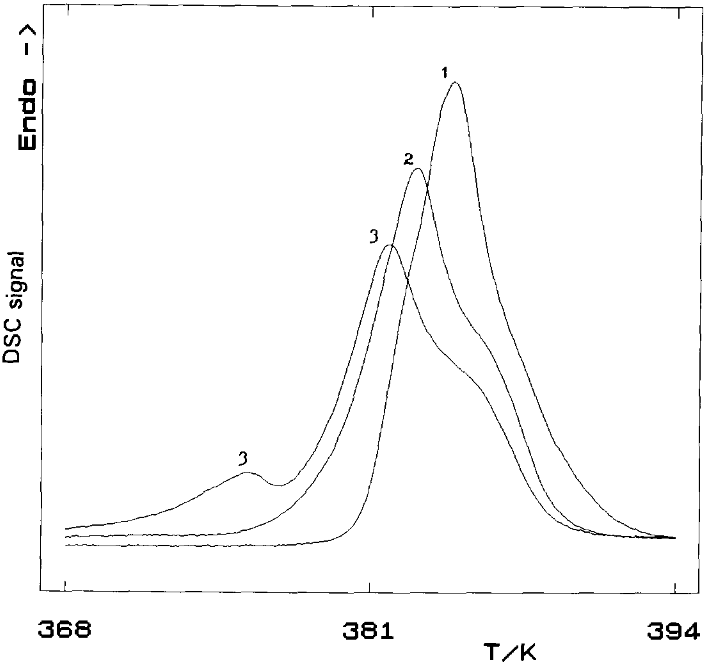

Fig. 1. Comparison of the consecutive DSC curves of sample I (A) at the beginning of the study ($t = 0$) and (B) after $t = 18\ 700$ h. The sample was used seven months after its synthesis and purification.

program [6] was used. The calibration was made using the following substances: gallium, indium, cadmium, lead, tin, zinc, naphthalene and benzoic acid. The purity of the metals used was greater than 99.999%, and that of the organic compounds greater than 99.95%. Temperature calibrations were determined by cryometric analysis.

Calorimetric measurements of the melting processes were performed using hermetic aluminium pans. The DSC curves were interpreted according to the procedure presented in Ref. [6]. All the measurements were executed using the same heating rate $\beta = 2$ K min^{-1}.

3. Results and discussion

Sample I of MBT was used about seven months after its preparation. Fig. 1(A) shows the DSC curves for the two consecutive melting processes for the same sample of MBT. The first curve possesses two maxima related to the two different endothermic processes. In the second run only one broad peak appears with the same peak temperature as the second peak of the first curve. The peak from the second run was taken to estimate the purity of MBT, which was $P = 91.2$ mol%.

The melting temperature of absolute pure MBT was $T_m^\circ = 393.4$ K; this temperature is consistent with the melting temperature taken from Ref. [7], $T_m = 392.0$ K. Three consecutive runs for sample I stored at room temperature for about two years are presented in Fig. 1(B). The purity estimated on the basis of the first peak of the first DSC curve was 99.2 mol% and the melting temperature was consistent with the temperature estimated from the first DSC curve presented in Fig. 1(A). This agreement indicates that the discussed peaks originate from the same process. The eutectic purity determined from the consecutive run was drastically low. Peak temperatures are shifted to lower temperatures, indicating the thermal decomposition of the solid. The second small peak appears in the third DSC curve, along with a broad peak at lower temperatures.

Sample II was obtained by additional purification of sample I. Two consecutive runs of sample II are shown in Fig. 2(A). The peak of the first run possesses an irregular shape from the beginning to the point of the complex melting process. The peak of the second run is broad and smaller than in the first DSC curve. The maximum is shifted to lower temperatures. Three consecutive scans of sample II, which had been stored over two years at room temperature, are shown in Fig. 2(B). The DSC curves possess two maxima. The peak temperatures of the consecutive

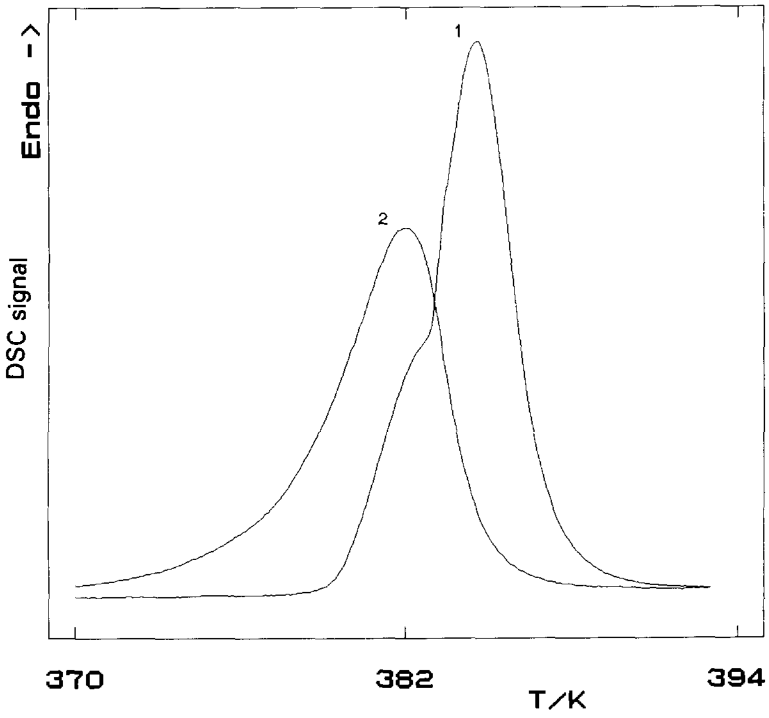

Fig. 2(A)

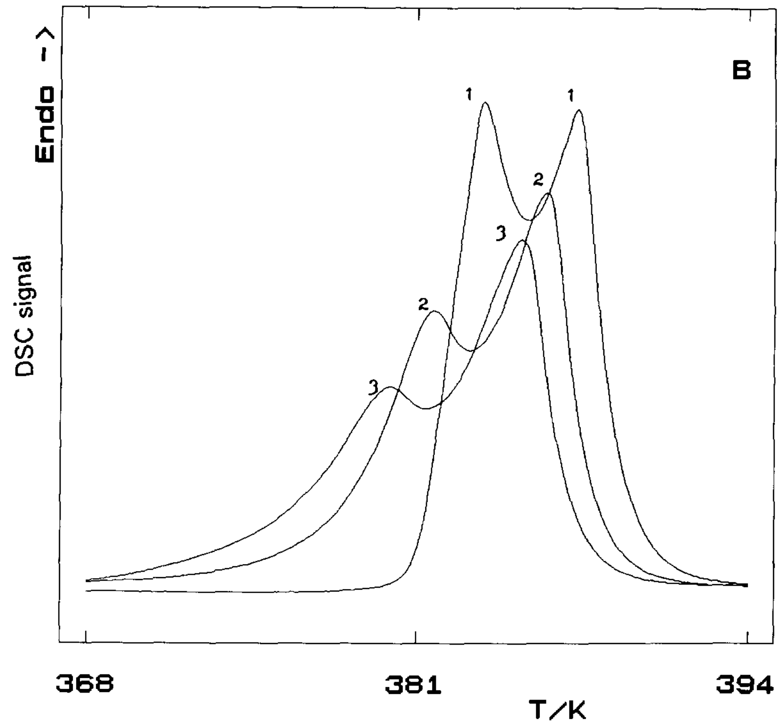

Fig. 2. Comparison of the consecutive DSC curves of sample II (A) at the beginning of the study ($t = 0$) and (B) after $t = 17\,300$ h. Sample II was obtained by additional purification of sample I.

DSC curves are shifted to lower temperatures. Changes in the first scan presented in Figs. 2(A) and 2(B) indicate that the very slow process proceeds in the solid stored at room temperature. The transition enthalpies and storage time at room temperature (counted for the time of the first calorimetric measurements) are collected in Table 1, columns 5 and 4, respectively. The transition enthalpy of sample II was higher than that measured for sample I, and the influence of storage time on both samples was also different. These differences are caused by the greater amount of impurities in sample I. Freshly synthesized and purified sample III was used after about one month for the measurements. Three consecutive scans for sample III are shown in Fig. 3(A). The first DSC curve possesses two peaks. The first peak temperature is consistent with the same temperature observed for samples I and II. The next DSC curves possess only one peak caused by the sample melting. This is the same situation as for sample I (see Fig. 1(A)). The purity estimated from the first measurment is $P_1 = 98.66$ and the melting temperature $T_m^\circ = 393.6$ K. The purities determined on the basis of the second and third melting processes are $P_2 = 98.39$ and $P_3 = 98.01\%$, respectively.

Table 1
Influence of the storage time of MBT on the enthalpy transition and transformation rates

Number of scans	Number of peaks	Time in h	ΔH in kJ mol^{-1}	x_A	$V^S_{A \to B} \times 10^5$ in mol% min^{-1}	P_E in mol%	V_E in mol% min^{-1}
I							
1	2	0	25.21	0.92	0.67	99.7	
2	1 [a]		18.47				
1	1 [b]	9936	25.83	0.88	0.57	99.1	0.15
2	2		22.30			97.7	
3	2		20.19				
1	1	18696	26.47	0.85		99.2	0.12
2						98.3	
II							
1	1 [b]	0	28.10	0.75	1.7	99.3	0.13
2			23.99			97.1	
1		6936	29.28	0.68			
1	1 [b]	7104	33.06	0.46		99.6	0.13
2	1 [b]		27.66			97.8	
1	1	8568	32.84	0.47		99.7	0.11
2			27.48			98.1	
1	2	17376	32.74	0.48		99.8	0.11
2	2		29.75			98.6	
3	2		27.17			97.3	
4	2		26.43				
III							
1	2	0	24.06	0.987	5.1		
2	1 [a]		22.30				
3	1 [a]		22.16				
1	2	1008	24.58	0.96	59.6	99.4	0.17
2	2		21.35				
1	2	1416	27.08	0.81	13.4	99.6	
2	2		25.65				
1	1 [b]	3288	28.44	0.73	1.1	99.6	
1	1 [b]	11988	29.4	0.68	5.3		
1	2	19200	33.20	0.45		99.8	0.14

[a] Melting of MBT. [b] Peak with several points of inflexion.

For unstable compounds the percentage rate of initial decomposition has been calculated on the basis of the purities (P_1,P_2), determined from two consecutive measurements performed with the same samples over time length (t_p), counted from the beginning of the melting process up to the end of the calorimetric measurement (removing sample from the calorimeter), as follows:

$$V = (P_1 - P_2)/t_p \tag{1}$$

It is assumed that the sample, being outside the calorimeter, crystallizes rapidly enough to stop the decomposition reaction. The upper limit of the melting fraction for purity determinations was $F \approx 0.25$. It was assumed that in this part of the melt, taking impurities into consideration, production was very low [6].

The mean rate of degradation calculated on the basis of the first and second melting processes is $V_{1/2} = 0.010\%$ min^{-1}, and for the second and third runs $V_{2/3} = 0.011\%$ min^{-1}. The successive DSC curves for the same sample III after 4.5 months storage at room temperature are presented in Fig. 3(B). The first DSC curve possesses a peak with one maximum, the second curve one with three maxima and the third curve one with two maxima. The total enthalpy transition increases observed for sample III during the storage time are listed in Table 1. The first DSC curves of sample III acquired for different storage time are shown in Fig. 4. The extrapolated onset temperature of the first peak is the same as for samples I and II. The temperatures of the second peak are shifted to the lower temperature region. The first run of samples I, II and III for storage times of over two years are presented in Fig. 5. The results suggest that molecules of form A (MBT) transform slowly to form B to produce a binary eutectic system. The eutectic melting temperature is $T^{\circ}_{\mathrm{mE}} = 380.3$ K. On the basis of the first measurement performed on sample III the melting enthalpy of form A was estimated, $\Delta H_{\mathrm{mA}} = 23.83$ kJ mol^{-1}.

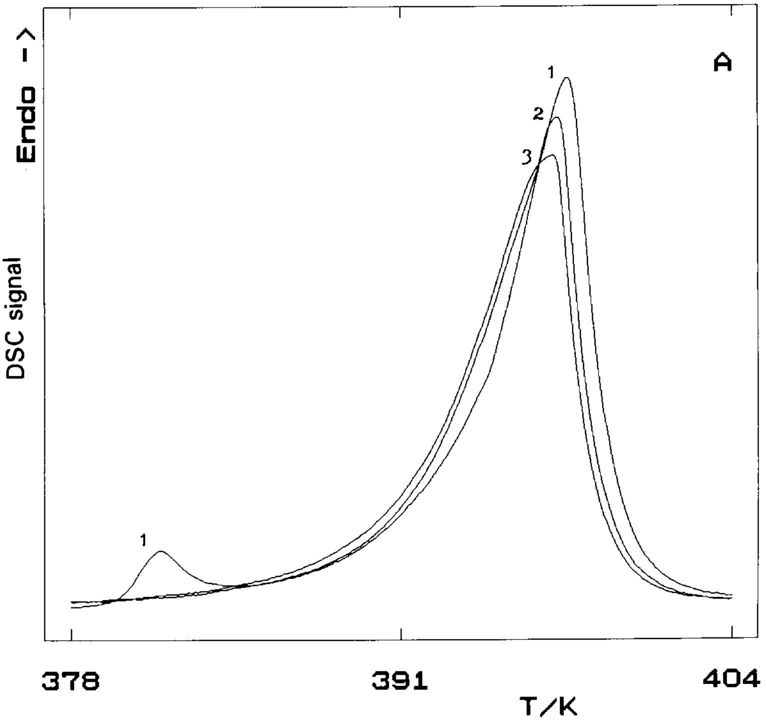

Fig. 3(A)

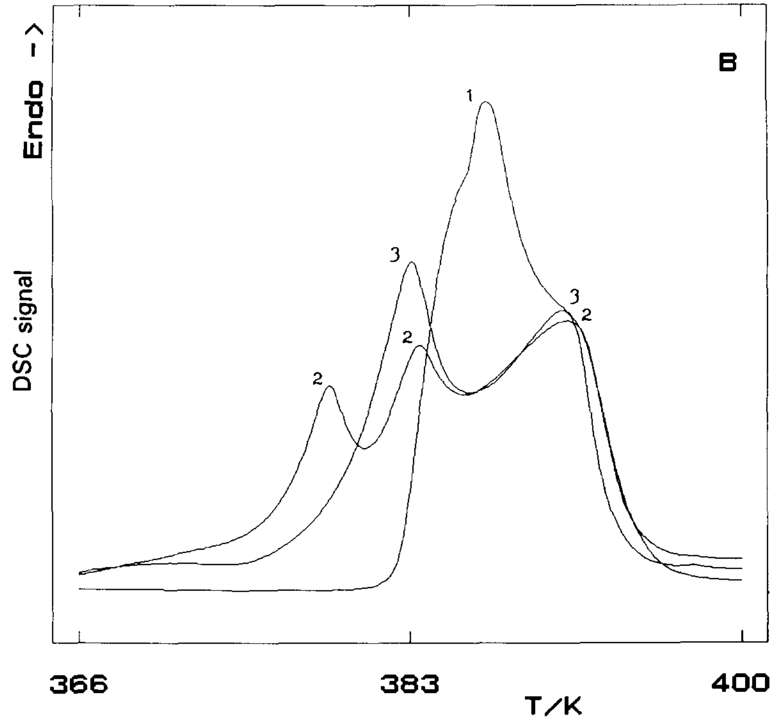

Fig. 3. Comparison of the consecutive DSC curves of sample III (A) at the beginning of the study ($t = 0$) and (B) after $t = 3300$ h. The sample was used one month after its synthesis and purification.

From the same measurements the melting enthalpy of form B (ΔH_{mB}) is estimated, assuming that forms A and B produce ideal solutions and the total transition enthalpy (ΔH) can be expressed as

$$\Delta H = \Delta H_{\mathrm{mA}} x_{\mathrm{A}} + \Delta H_{\mathrm{mB}}(1 - x_{\mathrm{A}}) \tag{2}$$

where x_{A} is the mole fraction of form A (MBT) determined by the cryometric method ($x_{\mathrm{A}} = P/100$), and $x_{\mathrm{B}} = (1 - x_{\mathrm{A}})$ is the mole fraction of form B. The estimated melting enthalpy of form B is 40.99 kJ mol^{-1}. This high value implies that the molecules of form B possess stronger molecular interactions in the crystal than in the case of form A. Eq. (2) allows estimation of the mole fractions of both forms in the investigated samples on the basis of the total enthalpy transition (ΔH) measured by DSC. The calculated mole fraction of form A in the sample I is $x_{\mathrm{A}} = 0.92$, which is consistent with the cryometric determination $x_{\mathrm{A}} = 0.912$ ($x_{\mathrm{A}} = P/100$). The melting temperatures of pure form A measured for samples I and III (see Figs. 1(A) and 3(A)) are consistent: $T^{\circ}_{\mathrm{m1}} = 393.4$; $T^{\circ}_{\mathrm{m3}} = 393.6$. The mole fractions x_{A} determined by Eq. (2) are collected in Table 1, column 6. The mole fractions of form A for all the investigated samples decrease on increasing the

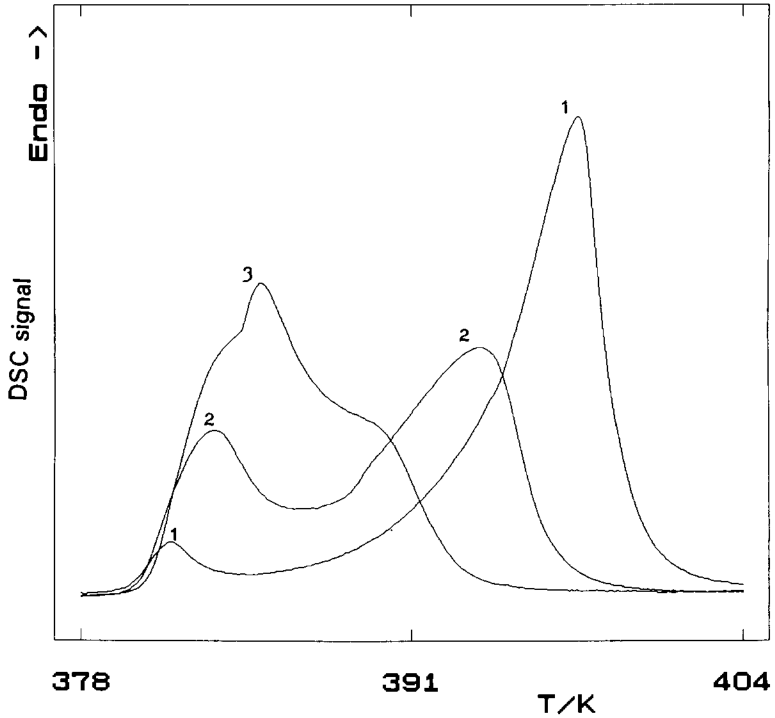

Fig. 4. Comparison of the first scan of sample III, after different storage times at room temperature (1) one month, (2) 2.5 months and (3) 5.5 months.

storage time. The additional purification of sample I shifted the equilibrium to form B in sample II. The final mole fractions of form A in samples II and III are consistent after over two years storage at room temperature ($x_A^{II} = 0.48$; $x_A^{III} = 0.45$). The mean initial rate of transformation of form A into B is calculated as the ratio of the change in mole fraction ($x_{A1} - x_{A2}$) to the differences in the storage times between two consecutive calorimetric measurements ($t_1 - t_2$):

$$\bar{V}_{A \to B} = (x_{A1} - x_{A2})/(t_1 - t_2) \tag{3}$$

Values of the mean initial rate of transformation are collected in Table 1, column 7. Large variations in the $\bar{V}_{A \to B}$ values result from experimental errors in the determination of the melting enthalpy. The peak transitions are complex and broad with composite baselines.

Assuming that the liquid mixtures of forms A and B create eutectic systems and the melting enthalpy of form A is temperature independent, a simple eutectic composition (x_{EA}) was estimated using the Schröder equation for ideal solubility:

$$-\ln x_{EA} = \frac{\Delta H_{mA}}{R}\left(\frac{1}{T_E} - \frac{1}{T_{mA}}\right) \tag{4}$$

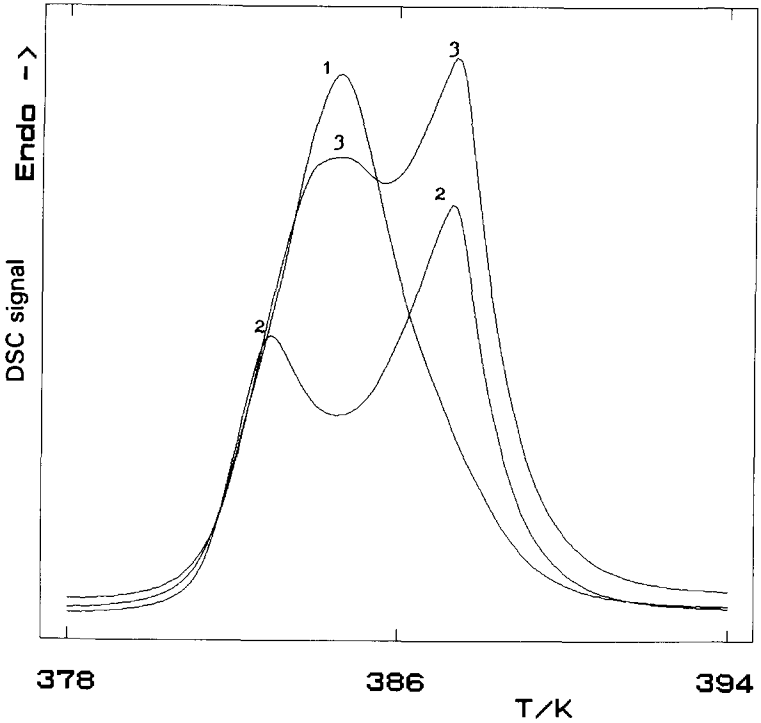

Fig. 5. Comparison of the first scans of the samples (I, II, III) for storage times of over two years at room temperature.

For estimation of x_{EA}, the mean value of the melting temperature of form A ($T_{mA} = 393.5$ K) and the mean values of the eutectic melting temperature ($T_E = 380.3$ K) were taken, giving $x_{EA} = 0.78$. Purities of the eutectic mixtures treated as pseudo-one component systems determined by the cryometric method are listed in Table 1, column 8. Decrease in purity with storage time at room temperature were not observed. These results imply that forms A and B are stable in the solid state. Chemical analysis proves that observed changes in the thermal ageing of MBT result from traces of water vapour forming the hydrate ($H_2O \cdot$ MBT); these traces of water were absorbed through a bottle well sealed from the surrounding atmosphere (relative humidity about 50%). Melting of the eutectic mixture of form A (MBT) and its hydrate (form B) is represented by the first peak on the DSC curve. The rate of transition from form A to form B is the rate of MBT hydration at standard conditions (MBT kept in a closed bottle). Purity changes in the eutectic mixture (pseudo-one component system) for consecutive melting processes are very high. The mean initial rates of decompositon of the eutectic compositions, V_E, calculated according to Eq. (1) are presented in Table 1, column 9. The mean value of the decomposition rate ($V_E = -0.14$ mol% min^{-1})

is over 10 times greater than the decomposition rate for pure form A (MBT) measured at the melting temperature. The high mean initial decomposition rate of the eutectic composition indicates that the MBT hydrate is more unstable than pure MBT. The thermal decomposition products are only formed in the liquid state above the eutectic temperature (see Figs. 1(B)–3(B)). Not taking into account the hydration phenomenon occurring in polar compounds containing water traces may lead to an entirely false interpretation of the experimental results. We will illustrate this conclusion using an example based on the results obtained in these studies. Protection against water traces and prediction of its influence on thermochemical properties is very difficult [8,9].

Acknowledgement

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