Kinetic study of solid–plastic transitions.
Part 2. Influence of experimental conditions

N. Sbirrazzuoli [a], Y. Girault [b] and L. Elegant [a]

[a] *Laboratoire de Thermodynamique Expérimentale, Université de Nice – Sophia Antipolis, Faculté des Sciences, BP 71, 06108 Nice Cedex-2 (France)*
[b] *Université de Nice – Sophia Antipolis, Faculté des Sciences, BP 71, 06108 Nice Cedex-2 (France)*

Abstract

The aim of this study is to incorporate the influence of different experimental conditions on the thermodynamic and kinetic parameters of the solid–plastic transition of pentaerythritol. The results show the importance of sublimation effects occurring with such phase change materials, which present a high vapour pressure and a low thermal conductivity. The influence on kinetic parameters and thermogram shapes is also discussed, and finally, a solution is proposed to overcome errors linked to the differential scanning calorimetry characterization of transformation of energetic materials, by proceeding to this analysis by means of a thermocouple located in the sample.

INTRODUCTION

Pentaerythritol crystals present in the solid state a transition that generates, by rotation from the low temperature phase (tetragonal), a new phase called the plastic phase (cubic), intermediate between the crystalline anisotropic phase and the liquid isotropic one. In the solid phase, the molecules are maintained by hydrogen bonds that are broken during the solid–plastic transition occuring near 186°C with a high transformation enthalpy ($300 \, J \, g^{-1}$).

In a previous study [1], we compared the capacities of different kinetic methods to model the phenomenon observed during differential scanning calorimetry (DSC) analysis of pentaerythritol solid–plastic transition. It is observed with such materials that the shape of the thermograms is very sensitive to the experimental conditions and this prompted us to study the effects of these conditions on thermodynamic and apparent kinetic

---

parameters of the solid–plastic transition occurring upon heating, with the help of the kinetic software previously described [2].

EXPERIMENTAL

High purity (more than 99%) 2,2-dihydroxymethylpropane-1,3-diol or pentaerythritol from Aldrich Chemical Company was used. All the scans were performed under nitrogen atmosphere with a Setaram DSC-111 differential heat flux calorimeter. The quantities previously defined [1] were used again (about 25 mg of pentaerythritol) except for sample **14** (123.2 mg). The modelling was also realized in a 20–80% interval, which led to accurate setting out for Arrhenius lines. The samples were packed, except for sample **12** which was used for comparison. Sample **13** is a mixture of pentaerythritol and aluminium powder (200 mesh), respectively 35% and 65% by mass, made at room temperature. Samples **2, 5, 8, 15** and **16** were made with a small hole in the crucible cover allowing the introduction of a platinel II thermocouple (0.28 mm diameter). The thermograms and/or the kinetic parameters of **4** and **4'**, **5** and **5'**, **14** and **14'**, **15** and **15'**, **16** and **16'** were obtained respectively from the programmed temperature and the temperature registered with the thermocouple placed in the sample.

RESULTS

Because the Šesták–Berggren model [3] makes physical interpretations of the kinetic exponents found and comparisons between several kinetic parameters obtained with different experimental conditions difficult, the method of Achar et al. [4], which also gives a good representation of the phenomenon [1] was selected to carry out these comparisons. The best representation is obtained by minimizing the difference (LSM) between experimental and computed thermograms [2]

$$\text{LSM:} \ \frac{1}{n} \sum_{i=1}^{n} (Y_i \, \text{exp} - Y_i \, \text{calc})^2$$

The results are summarized in Tables 1–5 and the different experimental effects on thermograms are shown in Figs. 1–4.

For samples of the same mass at the same scanning rate, we clearly noticed from Table 1 (**1** compared with **3**, **4** with **6** and **7** with **9**) that the use of sealed pans led to an increase in the material transformation rate, thus giving sharper thermograms. In a parallel manner, the enthalpy associated with the solid–plastic transition was always distinctly lower for open samples, with a difference of about 7% at 1, 2 and 5°C min^{-1} (see Table 1). At 10°C min^{-1}, the difference reached about 16% (transition enthalpies are 261.74 J g^{-1} and 310.00 J g^{-1} respectively with open and sealed pans). It is now clear that further applications should take into

TABLE 1

Enthalpies and kinetic parameters of the solid–plastic transition of pentaerythritol, from the programmed temperature, with method A of Achar et al. [4], $f(\alpha) = (1 - \alpha)^n$

Experimental conditions [a]	Sample	V [b] (°C min^{-1})	ΔH_{tr} [c] (J g^{-1})	n [d]	$\ln k_0$ [e]	E_a [f] (kJ mol^{-1})	R [g]	LSM [h]
O	1	1	286.67	1.0	258.98	1015.57	−0.99901	0.2945
TP	2	1	306.96	0.8	337.27	1317.14	−0.99917	0.3875
S	3	1	309.38	0.8	366.65	1429.71	−0.99923	0.6408
O	4	2	285.81	0.9	151.37	602.53	−0.99948	0.1676
TP	5	2	306.21	0.8	217.10	854.58	−0.99951	0.6341
S	6	2	302.93	0.8	238.77	937.15	−0.99939	0.7251
O	7	5	283.92	0.9	86.21	350.08	−0.99975	0.2798
TP	8	5	303.22	1.2	169.07	668.57	−0.99987	1.2812
S	9	5	307.26	0.9	128.87	514.52	−0.99978	1.1523

[a] O, Packed-open pans; TP, packed-closed pans using the thermocouple; S, packed-sealed pans; 20–80% interval; sample mass, about 25 mg. [b] V, scanning rate. [c] ΔH_{tr}, transition enthalpy. [d] n, kinetic exponent. [e] k_0, pre-exponential factor (s^{-1}). [f] E_a, activation energy. [g] R, correlation coefficient. [h] LSM fit of the experimental curve with the calculated one.

account the considerable sublimation of the material. In kinetic determinations, the use of sealed pans, in order to decrease the sublimation of the material, modifies the sample pressure, and this may affect kinetic calculations. We distinctly state that the open pans always allow the best description of the phenomenon from the kinetic parameters obtained.

It is noteworthy that when the scanning rate was increased, on samples treated under the same conditions, we observed a high decrease of the apparent activation energy E_a and $\ln k_0$ (k_0 is the pre-exponential factor) (Table 1). This effect is unusual: generally at low heating rates endothermic peaks are flatted when heating [5]. This observation suggests that the origin of the recorded phenomenon is relative not only to the material transformation but also to heat transfer in the sample.

TABLE 2

Enthalpies and kinetic parameters of the solid–plastic transition of pentaerythritol, from the programmed temperature, at 2°C min^{-1}, with method A of Achar et al. [4], $f(\alpha) = (1 - \alpha)^n$

Experimental conditions [a]	Sample [b]	ΔH_{tr} [c] (J g^{-1})	n [d]	$\ln k_0$ [e]	E_a [f] (kJ mol^{-1})	R [g]	LSM [h]
S	12	267.75	1.1	131.02	524.31	−0.99911	0.2710
S	13	302.44	1.8	451.75	1756.71	−0.99995	0.6658
TP	14	292.15	0.9	81.01	334.25	−0.99929	2.0385

[a] See footnote to Table 1. [b] 12, non packed-sealed; 13, packed-sealed PE-Al (35–65% in weight); 14, packed-closed, $m = 123.2$ mg. [c–h] See footnotes to Table 1.

TABLE 3

Kinetic parameters of the solid–plastic transition of pentaerythritol, from the programmed temperature, with method A of Achar et al. [4], $f(\alpha) = (1 - \alpha)^n$

Experimental conditions [a]	Sample	V [b] ($^{\circ}$C min^{-1})	n [d]	$\ln k_0$ [e]	E_a [f] (kJ mol^{-1})	R [g]	LSM [h]
TP	5	2	0.8	217.10	854.58	−0.99951	0.6341
TP	15	3	0.8	165.12	653.88	−0.99973	0.5606
TP	16	4	0.8	150.49	597.46	−0.99983	0.7108
				E_{a_m} [i] (kJ mol^{-1})	σ_{E_a} [j]	σ [k] (%)	LSM$_m$ [l]
				701.97	110.34	15.72	0.6351

[a,b,d–h] See corresponding footnotes to Table 1. [i] E_{a_m}, mean value of E_a. [j] σ_{E_a}, standard deviation. [k] σ, $\sigma E_a / E_{a_m}$. [l] LSM$_m$, mean value of LSM.

This view is supported by the influence of the low heat transfer observed in the experiments carried out with non-packed samples arranged in sealed pans (sample 12, Table 2). This sample disposition gave a high transition enthalpy decrease with a reduction of 12% at 2°C min^{-1} (compared to 6). It also involved a weaker transformation rate with flattened thermograms. To observe the influence of increasing the global thermal conductivity, pentaerythritol was mixed with aluminium powder (13). The transformation rate of the material was greatly increased by this addition (compared to 6) and the correlation coefficient R is, in this case, the best one observed.

In the same way, we observed a greater increase of the thermal gradient when the mass increased, between two samples (5 and 14, Tables

TABLE 4

Kinetic parameters of the solid–plastic transition of pentaerythritol, from the temperature registered with a platinel II thermocouple placed in the sample, using method A of Achar et al. [4], $f(\alpha) = (1 - \alpha)$

Experimental conditions [a]	Sample	V [b] ($^{\circ}$C min^{-1})	n [d]	$\ln k_0$ [e]	E_a [f] (Kj mol^{-1})	R [g]	LSM [h]
TP	5′	2	1.2	284.22	1112.67	−0.99544	10.5307
TP	15′	3	1.4	265.71	1040.43	−0.99857	5.9726
TP	16′	4	1.7	250.30	980.91	−0.99842	12.2281
				E_{a_m} [i] (kJ mol^{-1})	σ_{E_a} [j]	σ [k] (%)	LSM$_m$ [l]
				1044.67	53.87	5.16	9.5771

[a,b,d–h] See corresponding footnotes to Table 1. [i–l] See corresponding footnotes to Table 3.

TABLE 5

Kinetic parameters of the solid–plastic transition of pentaerythritol, obtained from the temperature registered with a platinel II thermocouple placed in the sample, using method B of Achar et al. [4], $f(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{1-1/n}$

Experimental conditions [a]	Sample	n [d]	$\ln k_0$ [e]	E_a [f] (kJ mol^{-1})	R [g]	LSM [h]
O	4′	1.1	157.13	627.26	−0.99706	0.9078
TP	5′	1.1	232.46	915.22	−0.99534	5.7812

[a,d–h] See corresponding footnotes to Table 1.

1, 2, Figs. 1, 2), recorded at the same scanning rate (2°C min^{-1}) and in the same conditions, associated with a large decrease of apparent E_a and $\ln k_0$.

Furthermore, it must also be considered that during the setting out of a thermogram, the power registered is drawn according to the programmed temperature of the differential scanning calorimeter. As mentioned by Rollet and Bouaziz [6] for DTA, thermograms established from the temperature of the block give almost the same results as that obtained from the time. In view of stressing, in addition to the importance of the parameters previously mentioned, the influence of the variation in temperature that can exist between the programmed value (T_{pr}) and the sample temperature, we experimented with a thermocouple introduced into the differential scanning calorimeter crucibles and placed in the
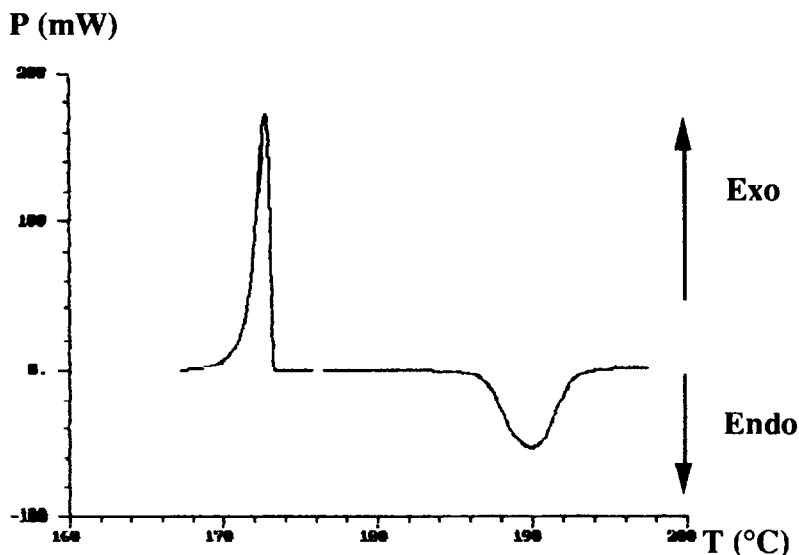
P (mW)

Fig. 1. Heating (endo) and cooling (exo) cycle of sample 5 (23 mg) at 2°C min^{-1}, from the DSC programmed temperature.

P (mW)
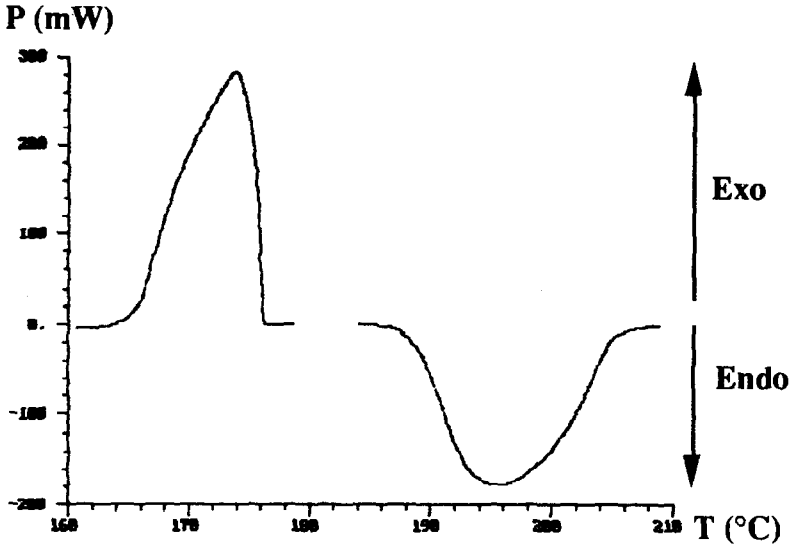

Fig. 2. Heating (endo) and cooling (exo) cycle of sample **14** (123.2 mg) at 2°C min^{-1}, from the DSC programmed temperature.

material. New thermograms were obtained afterwards according to the temperature of the thermocouple (T') (Figs. 3 and 4). The difference between the shapes of the two thermograms is the result of the difference between the temperature variation in the sample and the temperature programme of the DSC, the former being non-linear. As the basic reaction rate equation of kinetics can be applied for all the temperature
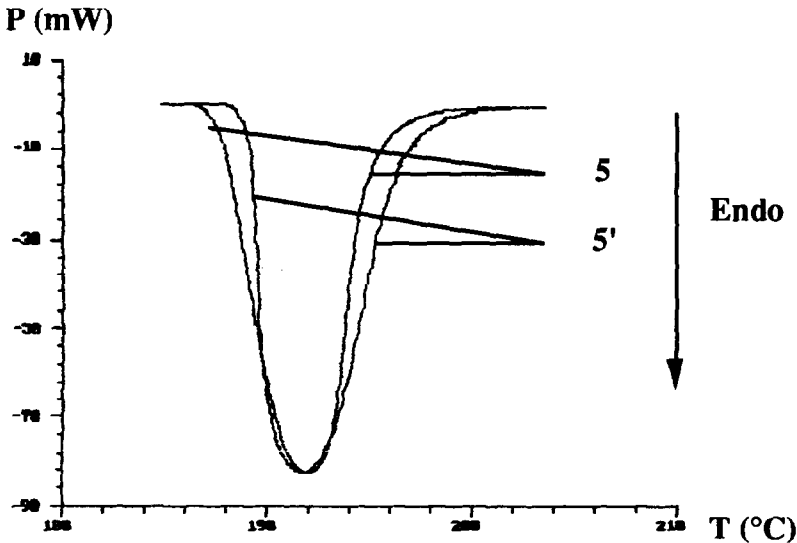
P (mW)

Fig. 3. Thermograms obtained from the programmed temperature (**5**) and from the thermocouple temperature (**5'**), for an identical sample (**5**) of PE (23 mg) at 2°C min^{-1}.

P (mW)

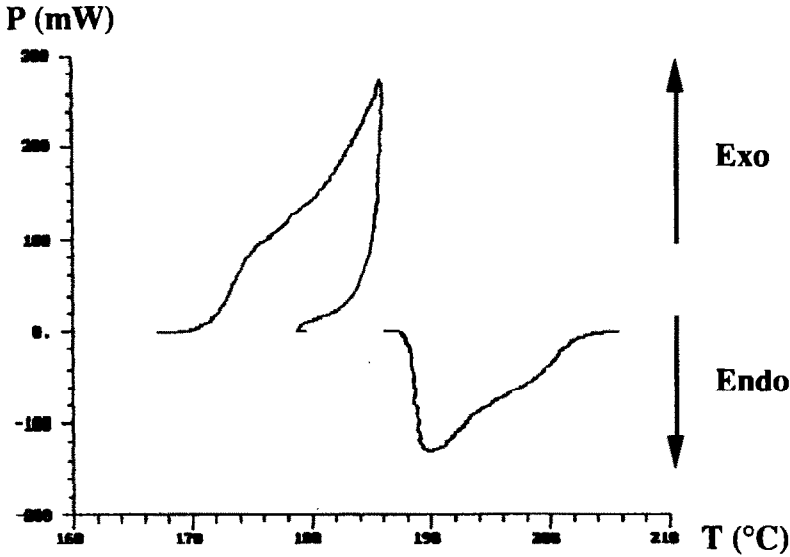Fig. 4. Heating (endo) and cooling (exo) cycle of sample **14'** (123.2 mg) at 2°C min^{-1}, from the thermocouple temperature.

variations and not only linear ones, as shown by Simmons and Wendlandt [7], kinetic parameters were obtained, by way of comparison, from a specific programme, using the same kinetic method and mathematical treatments but with computations made from the temperature of the thermocouple (compare Table 3 and 4).

The difference between parameters obtained for the same experimentation (**5** and **5'**, Tables 3 and 4) is important, the more so as the comparison takes place on the same recording, and as the quantity used (23 mg) was chosen with a view to limiting the problems linked to the thermal gradient. This can explain that with greater sample quantities, peaks drawn from the programmed temperature are flattened (Fig. 1 compared to Fig. 2) because of the time of propagation of the heat front.

Figure 4 shows that the "real" phenomenon is very fast at the beginning ($T < T_p$ the top of peak temperature) and is followed in the second part of the thermogram ($T > T_p$) by the heat front propagation whose extent depends on the quantity used. Furthermore, if the scanning rate is increased, the variation between programmed and sample temperatures is enlarged, the latter being, in this case, too, inferior to the former. This leads, as do greater sample quantities, to a decrease of the apparent parameters, the activation energy E_a and ln k_0. Taking into account these observations, the experiments shown in Tables 3 and 4 make it possible to compare the kinetic parameters obtained from the temperature T_{pr} and those from T'. For that study the variation of the scanning rate was reduced (2–4°C min^{-1}) for **5**, **15** and **16**. Even using the thermocouple temperature, the kinetic parameters are not constant at different heating

rates, but the variation is considerably reduced (see Table 4). It can be seen that σ (relative standard deviation) has been reduced from near 16% to only 5%. When using the thermocouple temperature, it is clear that taking into account the "self cooling" of the material induces an increase in the apparent activation energy and $\ln k_0$ (computed with an identical function) for kinetic methods using a single scan.

While for the experiments using the programmed temperature the best realization of the method of Achard et al. [4] was always obtained with a type A $f(\alpha) = (1 - \alpha)^n$ function, with the thermocouple temperature it was with the type B $f(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{1-1/n}$ function (sample 5', Tables 4 and 5), called the Johnson–Mehl–Avrami–Erofeyev–Kolmogorov equation [1]. In the latter case, Table 5 gives an example of the apparent kinetic parameters obtained with open pans and with sealed ones.

For the characterization of materials presenting a high transition enthalpy and a low thermal conductivity, and especially for kinetic studies, it is essential to use small quantities when operating with the programmed temperature, although the sample volume occupied is different from the available crucible volume. Therefore, Fig. 3 clearly shows that even with small sample quantities, the transformation kinetics of such material is different. Thus the evolution of heat flux versus programmed temperature cannot be used for the kinetic characterization of such materials.

Other plastic crystals studied, such as pentaglycerin and neopentylglycol also show identical variations in the shapes of thermograms.

CONCLUSIONS

Using the apparent activation energy and pre-exponential factor as modelling parameters of the DSC response, the experiments show the importance, in the analysis of such phase change materials, of the choice of the scanning rate, of sample quantities and of using packed samples. Thermal conductivity and sublimation effects induce a decrease in both the material transformation rate and the enthalpy involved. The results of the experiments also show a way of increasing the transformation rate of pure compounds.

Even with such precisely defined experimental conditions, the thermogram shapes are not representative of the real heat flux absorbed or released as function of the sample temperature. Experiments obtained from the thermocouple temperature confirm that the temperature variation in the sample is different from that imposed by the calorimeter and is not linear. Kinetic computations must take into account these temperature variations in DSC analysis of transformations of energetic materials. The use of a thermocouple is a solution proposed to overcome this problem.

Furthermore, we have observed, using thermocouple temperature, that the solid–plastic transition can be described with the help of the method of the Achar et al. [4]. The kinetic exponant and the mathematical function retained may correspond to a monodimensional growth of nuclei, controlled by the rate of propagation of the interface, but Malek's method modified by us [1] showed that the phenomenon is more complex. The first part of the thermogram ($T <$ top peak temperature) presents characteristics of a first order transition, while the second part is different from the one observed during melting, for instance, because the heat transfer in the liquid state is better than in the solid state.

Therefore thermograms obtained from the programmed temperature give rise to the well known question concerning these kinds of transformations, "What can make a first order transition appear non-isothermal?" Thermograms obtained from the thermocouple temperature (Fig. 4) correspond to a first order phenomenon, followed by the heat front propagation.

More generally, the comparison between thermograms obtained with or without thermocouple could be a way of selecting the proper scanning rate depending on the characteristics of each material studied (conductivity, transformation enthalpy, transformation kinetics) in order to compute kinetic parameters relative to the studied process.

In the future, we will deal with the transformation of pentaerythritol occurring upon cooling, where the use of the thermocouple temperature is even more useful.

REFERENCES

1 N. Sbirrazzuoli, Y. Girault and L. Elégant, Kinetic study of solid–plastic transitions. Part 1. Comparison of methods describing the transition, Thermochim. Acta, 202 (1992) 233.
2 N. Sbirrazzuoli, D. Brunel and L. Elégant, Different kinetic equation analysis (review), J. Therm. Anal., 37(11/12) (1991).
3 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
4 B.B. Achar, G.W. Brindley and J.H. Sharp, in Heller and Weiss (Eds.), Proc. Int. Clay Conf. Jerusalem, Vol. 1, 1966, pp. 67–73.
5 A.P. Rollet and R. Bouaziz, L'analyse Thermique, Tome 1, Les Changements de Phase, Gauthier-Villars, 1972, p. 66.
6 A.P. Rollet and R. Bouaziz, L'analyse Thermique, Tome 1, Les Changements de Phase, Gauthier-Villars, 1972, p. 70.
7 E.L. Simmons and W.W. Wendlandt, Thermochim. Acta, 3 (1972) 498.