KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF NITROGUANIDINE USING ACCELERATING RATE CALORIMETRY

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ABSTRACT

The thermal decomposition of nitroguanidine has been studied using accelerating rate calorimetry The experimental data have been treated by three methods to evaluate the activation energy and frequency factor Two methods using data gathered during the complete reaction yield very high activation energies while the value estimated using only the measurements in the initial stage of the decomposition is much lower Neither dilution of the sample with inert material nor substitution of nitrogen for air in the sample bomb had any significant effect on the rate of the decomposition Rate constants were compared with those reported in previous studies and it is concluded that a significant change in the mechanism of decomposition occurs in the neighbourhood of 160 ° C

INTRODUCTION

Nitroguanidine is an important ingredient in triple base propellants It exists in two forms, α and β, which melt at the sample temperature, 232° C, although higher melting points, 246 and 257° C, have been reported [1] DTA studies of Ripper and Krien [2] suggested that the α form begins to decompose at 187° C, while the β form decomposes at 205° C The density of the ordinary commercial nitroguanidine is about 0 3 g cm^{-3} Many tests concerning the properties of nitroguanidine have been performed by the U S Army Material Command [3]

From the thermal decomposition of nitroguanidine in the range 190–240° C, the main gaseous products are N_2O, H_2O, NH_3 and CO_2, accompanied by a large quantity of solid products Stals and Pitt [4] discussed the structure and reactivity of nitroguanidine and concluded that intramolecular hydrogen bonding was stronger than intermolecular hydrogen bonding They proposed a mechanism involving two pathways The first

decomposition pathway involved nitramide (NH_2NO_2) and cyanamide (NH_2CN) as intermediates, while nitrocyanamide ($HN-C\equiv N$, with NO_2 on the N) was the intermediate from the second pathway
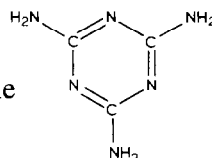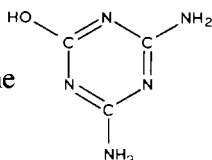
Studies of the decomposition by thermoanalytical techniques showed that a single exotherm occurred at 250°C [5] while a thermogravimetric study [6] showed that the initial weight loss began at 220°C Rogers [7,8] measured an activation energy for decomposition by the DSC technique of 21 kcal mol^{-1}

Volk [9] identified the solid products and analysed the gaseous products of nitroguanidine decomposition by mass spectrometry He found that N_2O and NH_3 were the main gaseous products and their ratio was temperature dependent The solid residue at 130°C, melamine and ammeline was analyzed using HPLC Up to 60–70% weight loss occurred during decomposition From the measurements of the rate of weight loss, an activation energy of 51 6 kcal mol^{-1} was obtained The decomposition was strongly affected by confinement

Taylor and Andrews, [10] used the flowing-afterglow spectroscopy technique to study the solid phase thermal decomposition reaction NH_3, H_2O, N_2O and CO_2 evolved from nitroguanidine were analysed by monitoring the emission of $NH^\star$, $OH^\star$, N_2O^+ and CO_2^+ Activation energies in the range 70–110 kcal mol^{-1} and correspondingly high frequency factors in the range 10^{30}–10^{50} sec^{-1} were obtained from the measurements of the rate as a function of temperature They suggested that autocatalytic evolution of gases may lead to violent decomposition above 160°C After this phenomenon occurred once, the activation energy reduced to 25–35 kcal mol^{-1}, with frequency factor in the range 10^5–10^7 sec^{-1}

Few studies of the kinetics of the decomposition have been attempted Because of the complexity of the reaction, the kinetic parameters which have been reported are difficult to interpret in terms of the mechanism of the decomposition The present work describes the decomposition of nitroguanidine in the accelerating rate calorimeter The effects of sample size, confinement of gaseous products, composition of the atmosphere and dilution have been investigated Methods for determining the activation energy from the data, following the equations derived by Townsend and Tou [11], were examined

EXPERIMENTAL

Apparatus

The accelerating rate calorimeter was introduced as an approach for hazard evaluation of exothermically reactive materials The container and the sample are maintained in an adiabatic environment Heat generated from the decomposition reaction does not dissipate to the surroundings and the decomposition proceeds as a self-accelerating reaction The instrument used in the present experiments was developed at Dow Chemical Company and manufactured by Columbia Scientific Industries of Austin, Texas A detailed description of the instrument design and operation logic can be found in the literature [11–14] Some modifications to the ARC to resolve problems in sample loading and pressure measurements have been described elsewhere [15,16]

The thermal decomposition of nitroguanidine was studied using the Hastelloy C, 1 inch diameter, spherical bomb with the filler tube of 3/16 inch O D and 1/2 inch length For the confined system, the bomb was connected to a pressure transducer and the pressure was monitored throughout the reaction For the non-confined system the bomb was only loosely connected to the transducer and the gaseous products were allowed to escape In most of the experiments the bomb was filled with air at atmospheric pressure Some experiments were performed in an atmosphere at N_2 The thermal inertia ranged from 9 4 to 23 4, obtained by using weights of sample between 0 2 and 0 5 g In some experiments nitroguanidine was diluted with silica in ratios 1 1, 1 2 and 1 5

Experiments were performed using the heat–wait–search method The sample and the container were first heated to 100°C and held for 30 min to ensure thermal equilibrium before the rate-search step After the wait period, it the self-heat rate is less than the detection limit, 0 02°C min^{-1}, the ARC proceeds automatically to the next preselected temperature When an exothermic reaction was detected, the calorimeter was maintained in an adiabatic condition and the measurements of time, temperature and pressure were collected and stored in the microprocessor

Materials

$$H-N-NO_2$$
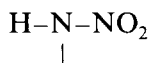
Nitroguanidine ($H N=C-NH_2$) with minimum purity 99% and average particle diameter 6 0–4 3 microns, was from Nigu Chemie, Waldkraiburg, West Germany The material was stored at room temperature with no further purification Silica, 240 mesh, was obtained from Fisher Scientific

RESULTS

Effect of confinement

In the confined system, the decomposition commenced between 161 and 165°C, depending on the values of the thermal inertia The time to maximum rate was short and the rate of pressure increase was fast The results are summarized in Table 1 and an example of the self-heat rate as a function of $1/T$ is shown in Fig 1 The total adiabatic temperature rise was in the range 15–17°C After reaction, the percent weight loss was approximately 60%

In the non-confined system, with sample size 0 25 g, the onset of decomposition was detected at about 200°C and the self-heat rate was slow The increase in temperature was too small to allow an analysis of the data and the results from these experiments were not considered further As observed in previous studies, confinement strongly affects the decomposition [9]

Effect of atmosphere

In these experiments the bomb was purged with nitrogen for 15 min, 30 min and 20 h respectively The results are included in Table 1 No difference in the results of these experiments and those under air atmosphere were observed Decomposition commenced about 161°C and the adiabatic temperature rise for the total calorimeter system, $\Delta T_{AB,s}$, was in the range of 14–18°C, depending on the values of the thermal inertia

These results show that oxygen does not affect the rate of decomposition, either through secondary reaction of reactive intermediates or through additional heat release from oxidation processes

Effect of diluent

To reduce the rate of decomposition and thereby improve the kinetic analysis, the sample was diluted with silica A 0 3 g sample of nitroguanidine was mixed with silica in ratios of 1 1, 1 2 and 1 5 After thorough mixing each mixture was tested individually by the step heat method in a confined system under air atmosphere

The thermal inertia, ϕ, is defined as follows

for a pure compound

$$\phi = 1 + \frac{M_b C_{vb}}{M_s C_{vs}}$$

for diluted material

$$\phi = 1 + \frac{M_b C_{vb}}{M_s C_{vs}} + \frac{M_d C_{vd}}{M_s C_{vs}}$$

TABLE 1

Thermal decomposition data of nitroguanidine under confined system

Expt no	Weight (g)	ϕ	$T_0{}^a$ (°C)	$m_0{}^a$ (°C min⁻¹)	$T_m{}^b$ (°C)	$m_m{}^b$ (°C min⁻¹)	$\Delta T_{AB,s}$ (°C)	E (kcal mol⁻¹)	log A (s⁻¹)
Air atmosphere									
165	0 2135	20 9	165 9	0 04	172 4	28 5	14 9	357	177
166	0 2540	17 7	161 0	0 02	170 1	21 0	17 3	276	136
231	0 2362	19 6	161 7	0 04	168 9	44 5	16 6	368	182
249	0 2228	21 2	166 6	0 09	175 2	10 8	12 8	314	154
250	0 2541	18 6	160 9	0 03	167 3	30 5	15 6	339	167
328	0 3074	15 1	160 9	0 03	171 2	25 5	18 0	302	149
N₂ atmosphere									
349	0 2119	23 4	161 2	0 03	169 8	15 5	14 1	258	127
350	0 2682	18 6	156 1	0 03	166 9	15 3	17 9	276	138
351	0 2153	22 6	161 5	0 04	172 1	8 8	14 6	303	149
Diluted with silica, air atmosphere									
Nitroguandine silica, 1 1									
358	0 6062	17 3	160 9	0 05	169 6	24 0	18 8	333	165
Nitroguandine silica, 1 2									
359	0 8866	18 7	161 0	0 07	169 1	19 0	17 3	321	159
Nitroguandine silica, 1 5									
360	1 7920	21 8	156 3	0 05	168 5	9 3	18 2	263	131

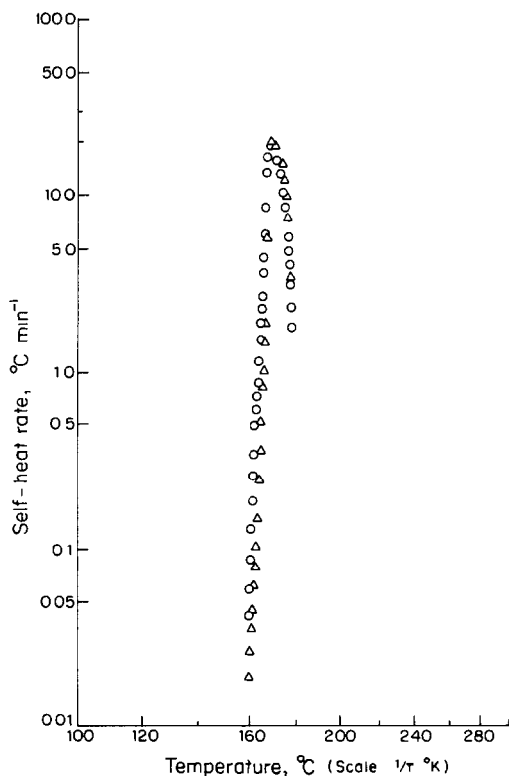[a] T_0, m_0, initial data
[b] T_m, m_m, data at maximum rate

Fig 1 Self-heat rate as a function of $1/T$ for nitroguanidine Confined system, air atmosphere △, $\phi = 17\,7$, ○, dilution of nitroguanidine with silica, 1 2, $\phi = 18\,7$

where M and C_v refer to mass and specific heat at constant volume respectively The subscripts b, s and d refer to bomb, sample and diluent, respectively

The results of one of these experiments is shown in Fig 1 and all the results are included in Table 1 Dilution with silica apparently had no effect on the pattern of decomposition

Calculation of the activation energy

In this study, the activation energy of decomposition of nitroguanidine was calculated following the three methods which were derived by Townsend and Tou [11] The experiments in the non-confined system had very short exotherms which did not provide enough data for the determination of the activation energy Only the data from the confined system were analysed

(a) *Calculation from* $k^\star$

The estimation of the Arrhenius parameters from the plot of $k^\star$ against $1/T$ was the simplest approach, since the curve was plotted automatically
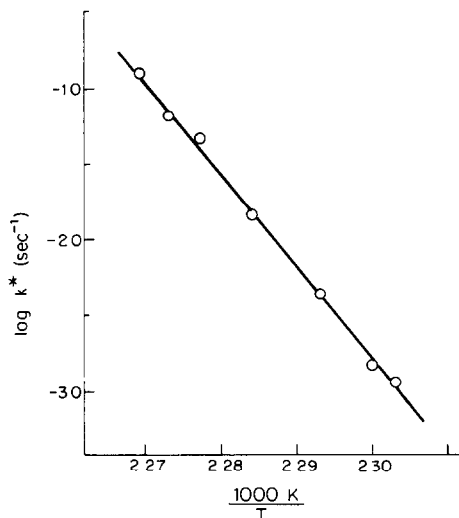
Fig 2 log $k^\star$ as a function of $1/T$ Confined system, air atmosphere, $\phi = 17\ 7$

from the microprocessor of the ARC Assuming a first order reaction, $k^\star$ is defined as

$$k^\star = \frac{m_T}{T_F - T}$$

where T is the temperature, m_T is the self-heat rate at that temperature and T_F is the final temperature In the decomposition of nitroguanidine, the self-heat rate increased very rapidly, giving a very steep slope, a high activation energy, and a correspondingly high value for the frequency factor The results are included in Table 1 and an example of an Arrhenius plot is shown in Fig 2

(b) *Calculation from time to maximum rate*

The relation between the time to maximum rate and the absolute temperature was discussed by Townsend and Tou [11] For reactions with activation energies greater than about 50 kcal mol^{-1}, the time to maximum rate, θ_m, could be expressed in the Arrhenius form

$$\ln \theta_m = \frac{E}{R}\left(\frac{1}{T}\right) - \ln A$$

where E is the activation energy, and A is the frequency factor The time to maximum rate was plotted as a function of $1/T$ and a typical result is shown in Fig 3 The slope was determined by linear regression The activation energies and the frequency factors determined by this method were in agreement with those obtained from method (a) with a similar range of uncertainty
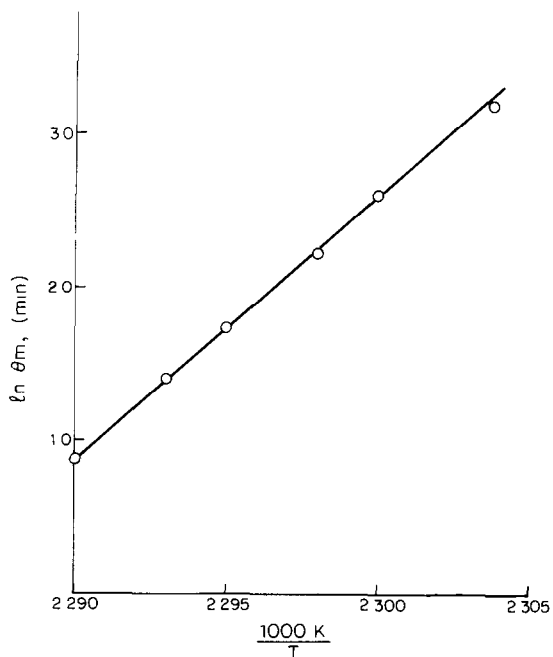
Fig 3 Time to maximum rate as a function of $1/T$ Hastelloy C bomb, confined system, air atmosphere, $\phi = 18\ 6$
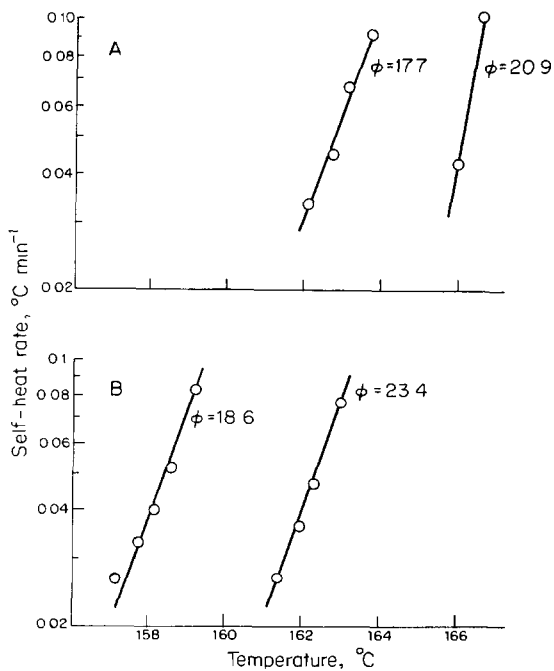

Fig 4 Self-heat rate as a function of temperature in the initial stages of the reaction Hastelloy C bomb, confined system (A) Air atmosphere (B) Nitrogen atmosphere

TABLE 2

Calculation of the activation energy for decomposition of nitroguanidine from the relation between the self-heat rate, the temperature and the thermal inertia

	Thermal inertia		Activation energy (kcal mol^{-1})
	ϕ_1	ϕ_2	
Air atmosphere	17 7	20 9	21 ± 1
N$_2$ atmosphere	18 6	23 4	22 ± 0 2
	18 6	22 6	17 ± 0 5

(c) *Calculation from the initial rate*

For determination of the activation energy by methods (a) and (b), data from the complete course of the reaction were used For method (c), also described by Townsend and Tou [11], only data from the initial stages of the reaction are used For this method temperatures are determined at constant self-heat rates for experiments with different values of ϕ For an accurate estimation of these temperatures, the self-heat rate is plotted as a function of temperature for each experiment Figure 4(A) shows these plots for the experiments under air atmosphere and Fig 4(B) shows the data obtained under N$_2$ atmosphere The activation energy was obtained from the equation

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{R}{E} \ln\left(\frac{\phi_1}{\phi_2}\right)$$

where T_1 and T_2 are the temperatures where a particular self-heat rate was observed with thermal inertias ϕ_1 and ϕ_2 respectively

From the smoothed curves, values of T_1 and T_2 were estimated for self heat rates of 0 03, 0 04, 0 05 and 0 06 °C min^{-1} The results are shown

TABLE 3

Measured activation energies for the decomposition of nitroguanidine

Technique	Temperature range (°C)	Activation energy (kcal mol^{-1})	Frequency factor, (log A (s^{-1}))	Reference
Flowing-afterglow	160–180	70–110	30–50	Taylor and Andrews [10]
	<160	25–35	5–7	
Isothermal	110–240	51 6	21 2	Volk [9]
DSC	200–204	20 9	7 5	Rogers [7]
ARC				Present work
	160–180	310 ± 50	155 ± 25	Method (a)
	160–180	300 ± 40	150 ± 20	Method (b)
	160–168	20 ± 2	–	Method (c)

in Table 2 Average values for the activation energy and frequency factor obtained by all three methods are given in Table 3

DISCUSSION

It is evident that application of methods (a) and (b) gives an activation energy very different from that obtained by method (c) Such high values for log A and E would in ordinary circumstances be dismissed as meaningless and possibly all values of the activation energy outside normal requirements for bond-breaking many be regarded as artificial Certainly, methods for extracting Arrhenius parameters from measurements of rates of decomposition made under non-isothermal conditions have been questioned [17–20] and have been shown to give erroneous results in some circumstances [21]

Most of the methods, including those used here, assume that the rate of decomposition follows an Arrhenius dependence on temperature, which implies that the decomposition follows the same path over the temperature range studied For methods (a) and (b) this range covers the complete course of the decomposition, whereas method (c) uses data from the initial stages only The large difference in activation energy therefore suggests that changes in the mechanism occur during the decomposition which have a marked effect on the rate These changes drastically alter the empirical Arrhenius parameters to the point where they no longer describe a statistical rate of passage over an energy barrier which can be related to bonds broken and formed during the reaction

Comparison of the present results with those obtained in previous studies by other methods, summarized in Table 3, reveals that a range of values almost as great as observed in the present experiments has been reported Interpretation of these results by comparison of the activation energies is of dubious value and instead we have made direct comparison of the rate constants

It appears that the results fall into two groups, shown in Figs 5(A) and (B), where the values of the rate constants are shown in the temperature range where they were measured The first group, shown in Fig 5(A), includes the average of the present results, the isothermal measurements [9] and two measurements of the rate of production of N_2O using the flowing-afterglow technique [10] The second group, in Fig 5(B), includes the remainder of the results of the measurements by the flowing-afterglow technique

Leaving for the moment the question of the significance of two groups of data, both sets suggest that the mechanism of the decomposition changes significantly at temperatures in the range 160–170 °C Both sets of data fulfil, within the uncertainty in the measurements, the condition outlined by Agrawal [22] which suggests a relation between the measurements from the
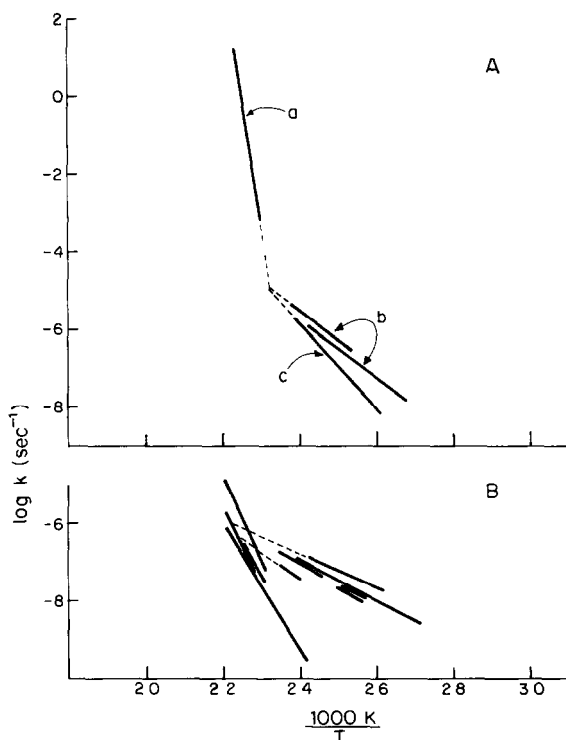
Fig 5 Arrhenius plots for rate constants for decomposition of nitroguanidine (A) a, present results, b, flowing-afterglow method (N_2O), c, isothermal experiments (B) Flowing-afterglow method

two ranges of temperature In both Figures data from the high and low temperature regions extrapolate to a common point of intersection From Fig 5(A) the point is 160°C and from Fig 5(B) the point is 170°C All the measurements, including those presented here, show that the change in the rate constant with temperature is much smaller at temperatures below 150°C than it is at temperatures above about 160°C The results reported by Volk [9], who analysed the products of the reaction over a wide range of temperature, indicated a similar change in mechanism He suggested that at low temperatures the products of the reaction inhibited the decomposition and that at higher temperatures ammonia and water caused an autocatalytic reaction

The rate constants derived from the measurements by the two techniques used in the high temperature range are nevertheless very different and a much more rapid increase in the rate with temperature was observed from the measurements of the decomposition in the ARC These differences very likely arise through the over-simplification of the methods used to derive the rate constants and not to fundamental differences in the mechanism of the decomposition in the high temperature region In the ARC the self-heating

causes a very rapid acceleration of the temperature and any effects of autocatalysis will be strongly magnified The Arrhenius parameters may not by themselves be directly interpreted in terms of a mechanism, but they do indicate the occurrence of a highly exothermic complex reaction [23]

Whether the difference between the two groups of data is significant or due only to experimental error, or error in derivation of the rate constants, cannot be resolved at this stage It seems apparent, however, that viewed separately, the individual measurements in Table 3 do not lead to any reasonable interpretation of the decomposition process, but taken together they suggest a related cause or a common process which manifests itself to different extents under different conditions of measurement

REFERENCES

1 T Urbanski, Chemistry and Technology of Explosives, Pergamon Press, Oxford, England, 1967, Vol 3, p 22
2 E Ripper and G Krien, Explosivstoffe, 17 (1969) 145
3 Anon Engineering Design Handbook, Headquarters, U S Army Material Command Pamphlet, AMCP 706-177, 1971, p 239
4 J Stals and M G Pitt, Aust J Chem, 28 (1975) 2629
5 Y P Carignan and D R Satriana, J Org Chem, 32 (1967) 285
6 M I Fauth, Anal Chem, 32 (1960) 655
7 R N Rogers, Thermochim Acta, 11 (1975) 131
8 R N Rogers, Thermochim Acta, 3 (1972) 437
9 F Volk, Propellants, Explosives, Pyrotechnics, 10 (1985) 139
10 G W Taylor and G H Andrews, Jr, Symposium on Chemical Problems Connected with the Stability of Explosives, Bastad, Sweden, 1979, p 297
11 D I Townsend and J C Tou, Thermochim Acta, 37 (1980) 1
12 J C Tou and L F Whiting, Thermochim Acta, 48 (1981) 21
13 M W Duch, K Marcali, M D Gordon, C J Hensler and G J O'Brien, Plant Operation Progress, AIChE, 1 (1982) 19
14 J M Pickard, J Hazardous Mat, 9 (1984) 121
15 P P Lee and M H Back, Thermochim Acta, 107 (1986) 1
16 P P Lee and M H Back, Thermochim Acta, 107 (1986) 17
17 A K Galwey, Thermochim Acta, 96 (1985) 259
18 R K Agrawal J Therm Anal, 31 (1986) 1253
19 J H Flynn, J Therm Anal, 27 (1983) 95
20 See discussions in Thermochim Acta, 110 (1987) J H Flynn, M Brown and J Sestak, 101, T Kemeny 131, P D Garn, 141, M Maciejewski and A Reller, 145
21 J P Elder, J Therm Anal, 30 (1985) 657
22 R K Agrawal, J Therm Anal, 31 (1986) 73
23 J H Flynn, Thermochim Acta, 37 (1980) 225