

## Safety and stability studies on isosorbide dinitrate (ISDN)

G.Om Reddy and A. Srinivasa Rao

*INBRI Division, IDL Chemicals Limited, P.B. No. 397, Malleswaram, Bangalore 560 003 (India)*

(Received August 30, 1991; accepted in revised form March 4, 1992)

### Abstract

A detailed study on pure, crude, acidified and diluted isosorbide dinitrate (ISDN) was carried out to evaluate thermal stability and explosive sensitivity by using differential scanning calorimetry (DSC), thermogravimetry (TG) and cap sensitivity experiments. The results indicate that thermal stability of pure ISDN is as good as pentaerythritol tetranitrate. Acidity, especially sulphuric acid, adversely affect the stability, whereas dilution with water or lactose did not affect the thermal stability. However, the dilution effect is clearly seen in explosive sensitivity and thermal decomposition energy. ISDN diluted with 30% water behaves like a non-explosive. Acid influence on the decomposition kinetics is also studied in detail. A considerable decrease in energy of activation ( $E_{act}$ ) is noticed when ISDN is contaminated with sulphuric acid, whereas lactose addition increases the activation energy. A plausible explanation is provided for the change in activation energy. A good correlation is observed between the experimentally obtained activation energy and the length of the O-N bond derived from modified neglect differential overlap (MNDO) calculations.

---

### 1. Introduction

Isosorbide dinitrate (ISDN) belongs to a group of vasodilator drugs called nitrates. Related to glyceryltrinitrate and pentaerythritol tetranitrate (PETN), it is most often used to relieve the pain and frequency of angina attacks [1]. It is also used with other drugs for the control of certain type of heart failure. ISDN is fast-acting and the effects are longer lasting than some other nitrates. Unlike glycerylnitrate, ISDN can also be stored for long periods of time without losing its effectiveness.

Pure ISDN, a white crystalline material, has proven to be a powerful explosive and is, therefore, diluted with lactose or other suitable diluents to make handling, transportation and storage safer for pharmaceutical purposes. The

---

*Correspondence to:* Dr. G.Om Reddy, Standard Research Centre, 7-1-27, Ameerpet, Hyderabad 500016, Andhra Pradesh (India).

normal dilutions used for pharmaceutical preparations are 25% ISDN with 75% lactose or 40% ISDN with 60% lactose.

In view of the explosive hazards associated with ISDN, a detailed study on the safety aspects of ISDN was warranted to educate and warn the users of this material, especially drug manufacturers. This paper discusses in detail the thermal sensitivity and stability of pure and acidic ISDN and ISDN diluted with lactose. Decomposition kinetics, decomposition energy and the explosive properties of dry and wet ISDN were also examined. Previously Mohan Murali et al. [2] from our laboratory published the hazardous characteristics of ISDN-lactose mixtures. The Chemical Thermodynamic and Energy Release Evaluation Program of ASTM [3] (CHETAH) rated pure ISDN as a high hazard 25/75 ISDN-lactose mixture as low hazard and 40/60 ISDN-lactose mixture as medium hazard.

## 2. Experimental

### 2.1 Equipment

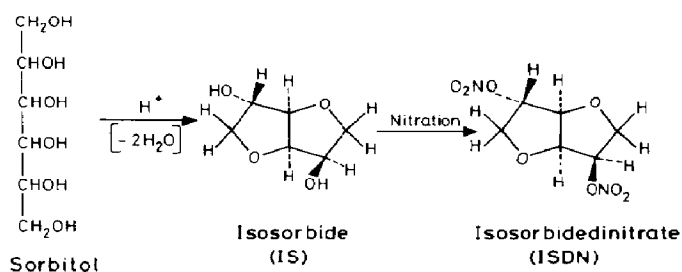
Perkin-Elmer DSC-2C and Perkin-Elmer TGS-2 were used for thermal study. The experiments were carried out under non-isothermal conditions with a constant flow of nitrogen gas. The samples were crimped in aluminium pans with a pin hole on the lids. Thermograms were recorded using percent mode which directly reads the loss of weight (%) with temperature. The sample size was kept in the range of 2-4 mg for all differential scanning calorimeter (DSC) and thermogravimetry (TG) experiments.

Cap sensitivity experiments were carried out in a sound proof bomb using a No. 6 detonator. The Nicholet digital oscilloscope 2090 series was used for measuring detonation velocity and carbon resistor probes were used for sensing the detonation wave.

### 2.2 Material

ISDN was prepared in our laboratory by a known procedure [4] as shown in Scheme 1 and recrystallised from acetone/water mixture to obtain pure ISDN.

A known quantity of lactose was added to pure ISDN and mixed well using agate mortar carefully to make various mixtures. (Caution: pure ISDN is hazardous to grind in a mortar.) Known quantities of sulphuric acid (10%) and nitric acid (10%) were added separately to pure ISDN and mixed thoroughly using mortar and pestle. For explosive sensitivity experiments, the material, after mixing with water, was packed in 25 mm plastic tubes and densities were determined before firing.



Scheme 1. Preparation of ISDN.

### 3. Results and discussion

#### 3.1 Thermal sensitivity

DSC is a very useful technique for the evaluation of thermal sensitivity/stability of a hazardous material. DSC thermograms of pure and crude ISDN and pure ISDN diluted with 60% lactose were recorded and displayed in Fig. 1. Pure ISDN showed a melting point of 340 K and a sharp decomposition exotherm with an onset temperature of 443.0 K, whereas a crude sample showed a melting point of 335.0 K and a broad decomposition exotherm with an onset temperature of 427.0 K. ISDN diluted with lactose exhibited, in addition to ISDN melting peak at 340.0 K, another broad endotherm around 412.0 K (due to water loss). There is no change in the decomposition temperature of ISDN due to lactose dilution; but the decomposition portion of thermograms splits into two; and the area under the curve, which is the measure of decomposition energy, is drastically reduced. It may be appropriate to state here that lactose dilution does not influence the thermal stability of ISDN, but certainly minimises the exothermicity of ISDN due to dilution effect. The thermal properties are listed in Table 1.

A detailed study was carried out on various compositions, wherein the lactose dilution was increased from 5 to 75 wt%. A few DSC thermograms recorded with 10 K min<sup>-1</sup> heating rate are presented in Fig. 2. The melting temperatures and decomposition temperatures are listed in Table 1. It is interesting to note that the melting point of ISDN is not affected by lactose dilution.

The DSC thermogram of pure lactose shows two sharp endotherms, one in the temperature range of 420–430 K and another in the temperature range of 480–500 K. The former peak is due to the loss of a water molecule (monohydrate) present in lactose and the latter peak is due to lactose decomposition. For up to 20% lactose in ISDN the first peak due to loss of lactose water was not noticeable, whereas more than 30% lactose dilution exhibited very broad endotherms. In fact ISDN influenced the dehydration of lactose and advanced the endothermic peak by about 20 K. Lactose did not influence the decompo-

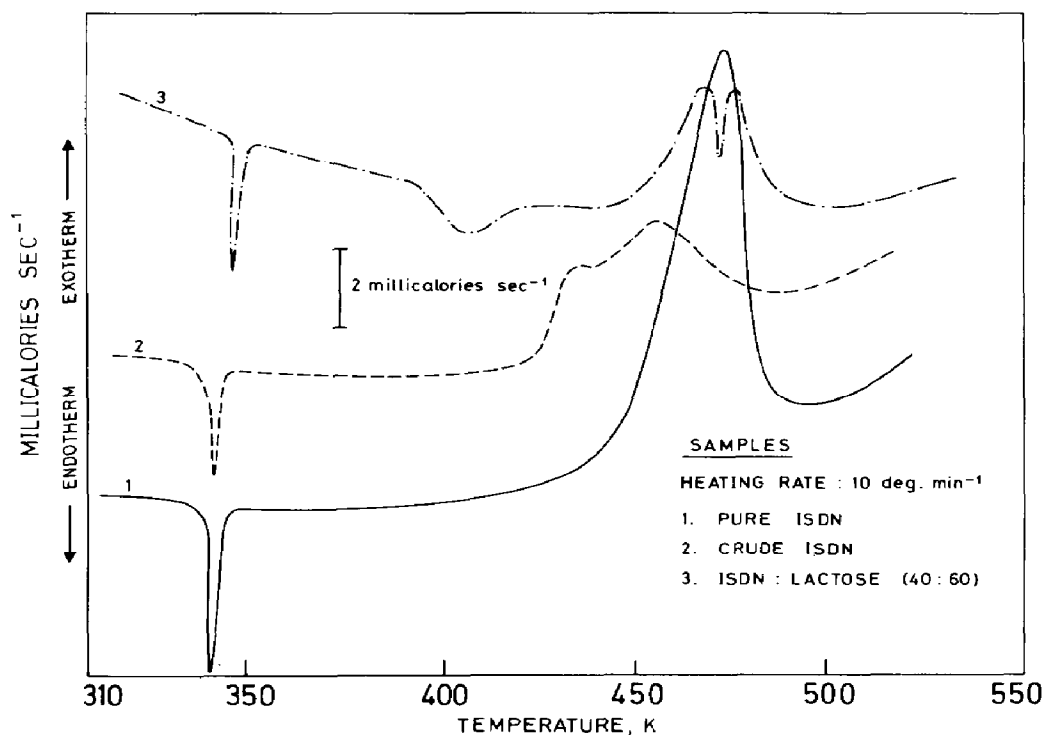


Fig. 1. DSC thermograms of (1) pure ISDN, (2) crude ISDN, and (3) 40/60. ISDN-lactose mixture.

sition temperature of ISDN, but considerably reduced the decomposition energy by acting as a heat sink. It is apparent that ISDN influenced the decomposition of lactose and was also advanced by about 20 K. Up to 20% lactose dilution ISDN showed a sharp single decomposition peak, whereas 25–35% of lactose showed a shoulder in decomposition while more than 35% lactose showed a clear split in the ISDN decomposition peak (Fig. 2). Thus, the dilution of ISDN with lactose reduces the exothermicity and enhances the safety of ISDN handling.

The split in the exotherm of ISDN lactose mixtures had given an impression that the decomposition is a two-stage process. As mentioned earlier, lactose decomposition is endothermic in nature. In diluted samples, ISDN and lactose decompose simultaneously. Decomposition due to ISDN is heat producing, while lactose decomposition is heat absorbing. The shaded areas of curves 4, 5 and 6 (Fig. 2) are due to an endothermic decomposition of lactose, which occurs during the exothermic decomposition of ISDN.

### 3.2 Decomposition energy

DSC is a quantitative technique to determine the enthalpy of decomposition. The area under the curve is directly related to the amount of heat released.

TABLE 1

## Thermal sensitivity

Sample	Endotherms (K)		Exotherms (K)			
			$T_i$	$T_p$	$T_e$	
Pure ISDN	340.0	-	443.0	467.0	-	482.0
Crude ISDN	336.0	-	427.0	452.0	-	480.0
ISDN/lactose (95/5)	340.0	-	445.0	468.0	-	482.0
ISDN/lactose (90/10)	340.0	-	445.0	468.0	-	482.0
ISDN/lactose (85/15)	340.0	-	444.0	468.0	-	482.0
ISDN/lactose (80/20)	340.0	-	443.0	468.0	-	481.0
ISDN/lactose (75/25)	339.0	-	443.0	468.0	-	480.0
ISDN/lactose (70/30)	340.0	-	444.0	468.0	-	481.0
ISDN/lactose (65/35)	340.0	Not clear	445.0	468.0	-	482.0
ISDN/lactose (60/40)	340.0	400.0 <sup>a</sup>	445.0	463.0	469.0	488.0
ISDN/lactose (50/50)	340.0	400.0 <sup>a</sup>	446.0	463.0	469.0	487.0
ISDN/lactose (40/60)	340.0	401.0 <sup>a</sup>	448.0	463.0	470.0	485.0
ISDN/lactose (25/75)	340.0	401.0 <sup>a</sup>	447.0	463.0	473.0	487.0
Pure lactose	420.0	477.0 <sup>b</sup>	-	-	-	-

<sup>a</sup>Lactose water loss.

<sup>b</sup>Lactose decomposition.

$T_i$ , Initial temperature,  $T_p$ , peak temperature, and  $T_e$ , end temperature.

High purity indium (99.9% pure) was used as a standard for estimating the decomposition heat energy of ISDN and various ISDN-lactose mixtures. Two dilutions of ISDN-lactose, 40/60 and 25/75, are commonly used for pharmaceutical preparations. The estimated decomposition energy values are listed in Table 2. Crude ISDN showed less energy compared to pure ISDN. The decomposition energy decreased as the lactose percent in ISDN mixtures increased (Table 2). Though the lactose decomposition energy is very small ( $165.00 \text{ J g}^{-1}$ ), its influence on ISDN decomposition is very remarkable. This study clearly indicates that ISDN diluted with lactose is less energetic and safer to handle than when pure. The common dilutions of ISDN-lactose, 40/60 and 25/75, are quite safe and their decomposition energies are 1/5 and 1/6 of pure ISDN, respectively.

### 3.3 Kinetics of decomposition

The kinetics of decomposition play a very important role in the assessment of the hazardous property of energetic materials. The activation energy helps in rating the hazardous potential of a given explosive. The higher the activation energy, the safer the material is to handle.

There are several methods for calculating kinetic parameters. We restricted our study to non-isothermal analysis, the Ozawa method [5], which is also the ASTM method used. The activation energy obtained by this method is inde-

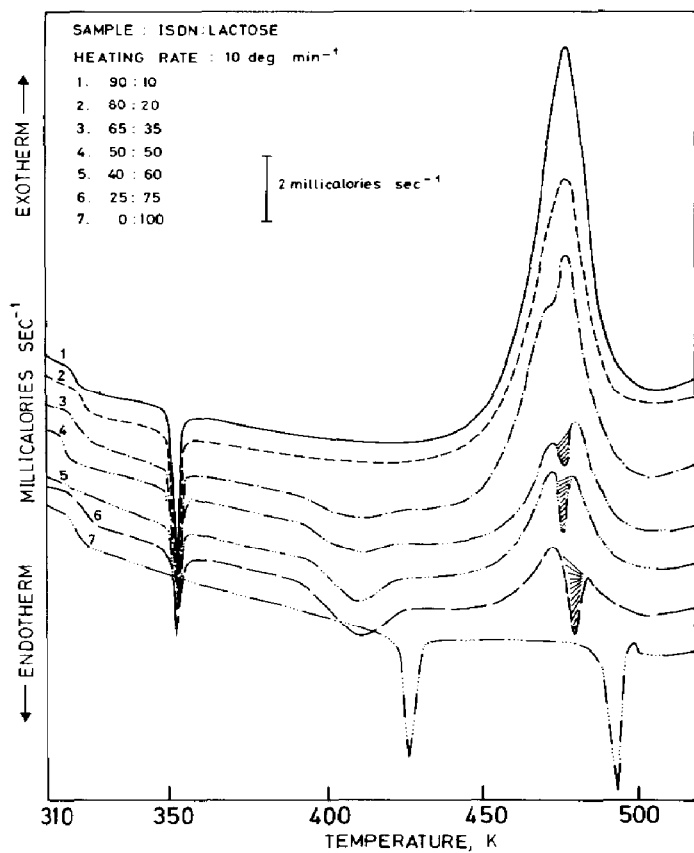


Fig. 2. DSC thermograms of ISDN-lactose mixtures.

TABLE 2

Heat of decomposition

ISDN	Lactose	Found (J/g)	Calculation for dilution (J/g)	Stabilisation (J/g)
100	0	2319.0	2319.0	0.0
95	5	2291.0	2195.0	96.0
90	10	2167.0	2071.0	96.0
85	15	1890.0	1946.0	-56.0
80	20	1815.0	1822.0	-7.0
50	50	712.5	1077.0	-365.0
40	60	505.0	829.0	-324.0
25	75	403.0	456.0	-53.0
0	100	165.0	-165.0	-

pendent of the order of the reaction. This method depends on the fact that the reaction rate depends upon the heating rate, in cases where self-heating occurs during decomposition. An increase in the heating rate shifts the peak temperature to a higher temperature. The reaction rate is maximum at peak temperatures. By this method a plot of  $\ln(\phi)$  versus reciprocal absolute peak temperature will produce a straight line with a slope equal to  $-E/R$  [5].

Pure ISDN, crude ISDN and ISDN-lactose (40/60) are subjected to various heating rates (5, 10, 20 and 40  $\text{K min}^{-1}$ ) and the thermograms are shown in Figs. 3, 4 and 5, respectively. Melting and decomposition temperatures are listed in Table 3. While there was no influence of heating rate on the melting point of crude and pure ISDN, a slight shift to higher temperature was observed in the case of ISDN-lactose mixtures with increased heating rates. However, there was a clear shift in the decomposition curves. Pure ISDN showed sharp peaks, whereas crude ISDN showed broad peaks with a shoulder and ISDN-lactose mixture exhibited two peaks, Peak 1 ( $T_{p1}$ ) and Peak 2 ( $T_{p2}$ ) (Table 3). The plots of  $\ln(\phi)$  vs reciprocal peak temperatures are shown in Fig. 6, and activation energy ( $E_{act}$ ) values are listed in Table 4. It is very clear from the activation energy values that crude ISDN is most hazardous and the

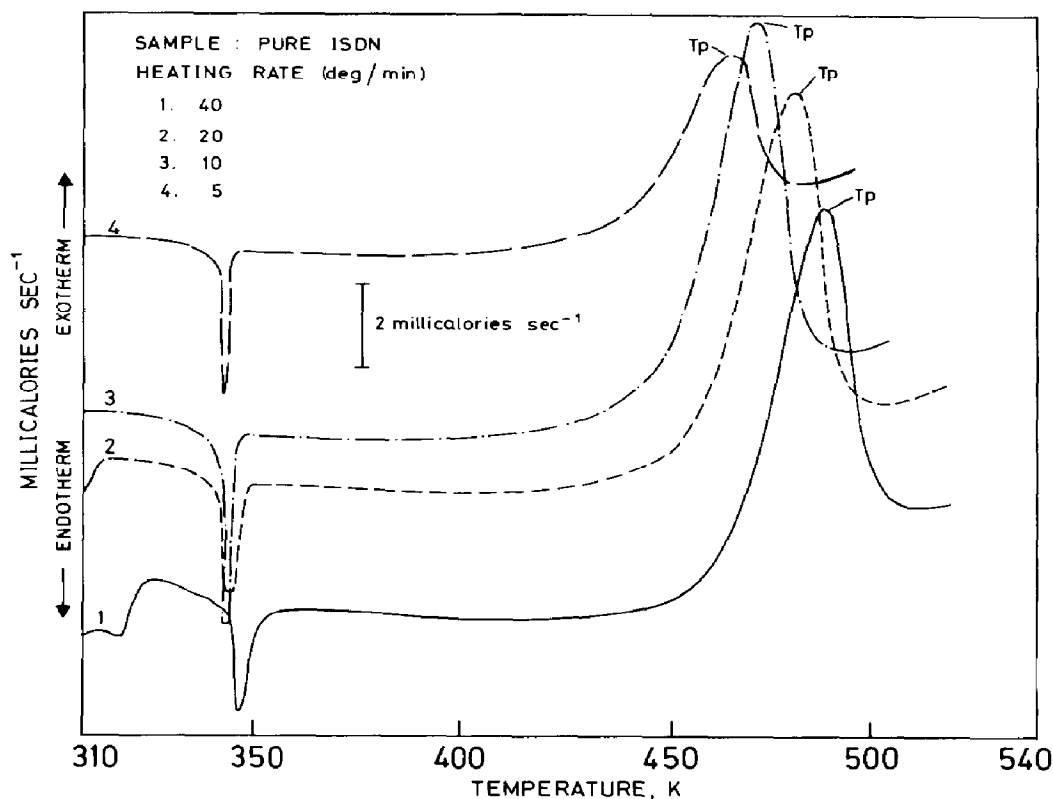


Fig. 3. Effect of heating rate on pure ISDN.

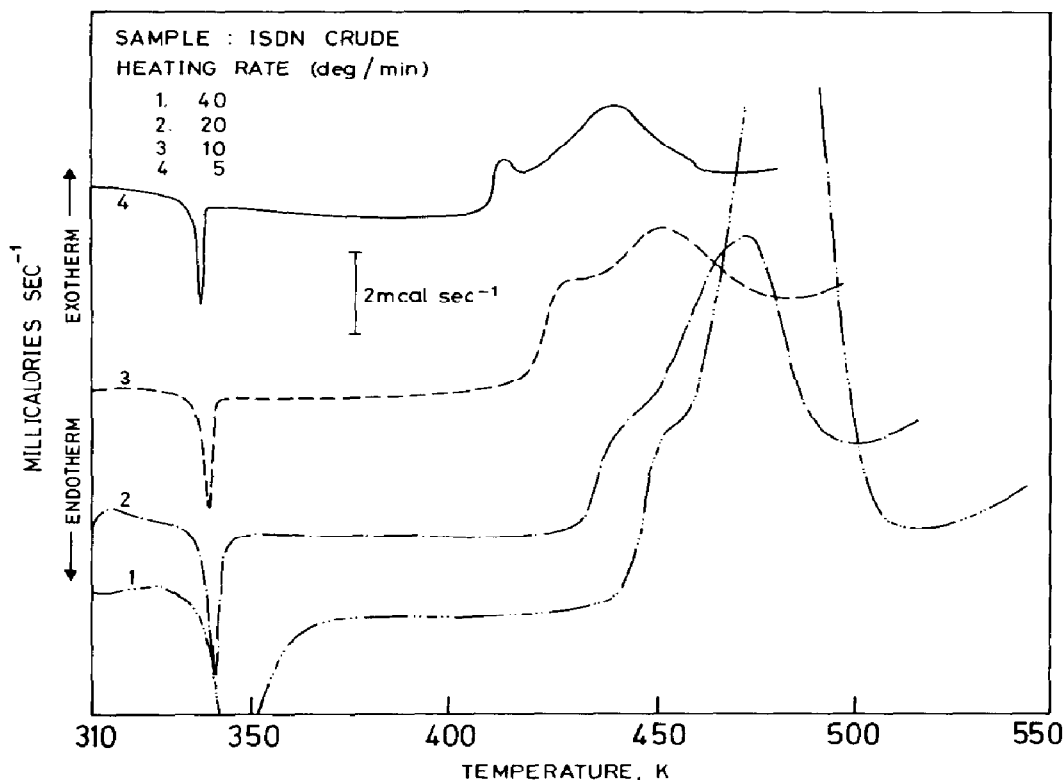


Fig. 4. Effect of heating rate on crude ISDN.

ISDN-lactose mixture is least hazardous, whereas pure ISDN falls in between. The decreasing order of hazard is given below:

Crude ISDN > pure ISDN > ISDN/lactose (60/40).

The common ISDN/lactose mixtures, 40/60 and 25/75, would be safer than the 60/40 mixture.

### 3.4 Thermogravimetric analysis

Weight loss measurements were carried out on pure, crude and lactose diluted ISDN. The TG thermograms of pure and crude ISDN with 10 K min<sup>-1</sup> heating rates are shown in Fig. 7. Pure ISDN showed rapid weight loss compared to crude ISDN. This observation supplements previously discussed DSC data. The weight loss was in the range of 85-95%.

Ozawa [6] developed a method for the estimation of activation energy for TG analysis which states that the logarithm of the rate of heating ( $dT/dt$ ) has a linear relationship with the reciprocal of the absolute temperature for the given conversion ( $\alpha$ ), regardless of the order of reaction. This method requires non-isothermal runs at different heating rates.



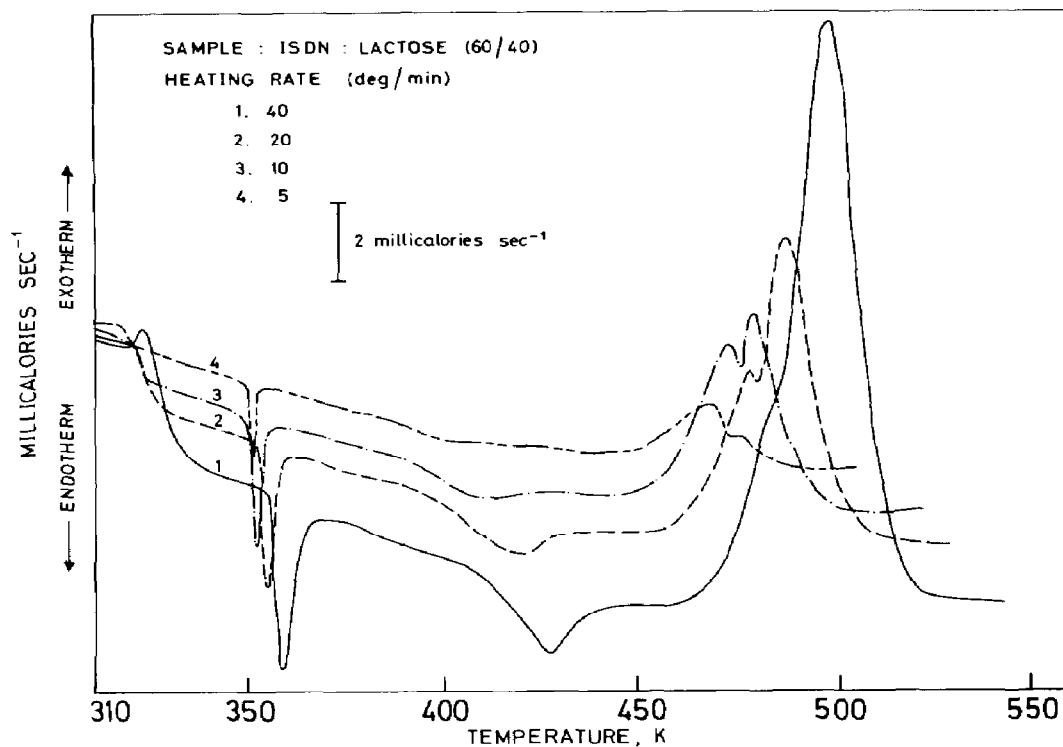


Fig. 5. Effect of heating rate on ISDN-lactose (60/40) mixture.

TABLE 3

Effect of heating rate

Sample	Heating rate (K/min)	Peak temperature (K)	
Pure ISDN	5	-	458.0
	10	-	467.0
	20	-	475.0
	40	-	481.0
Crude ISDN	5	-	440.0
	10	-	452.0
	20	-	472.0
	40	-	483.0
ISDN/lactose (60/40)	5	458.0	465.0
	10	462.0	468.0
	20	467.5	476.0
	40	-	485.0

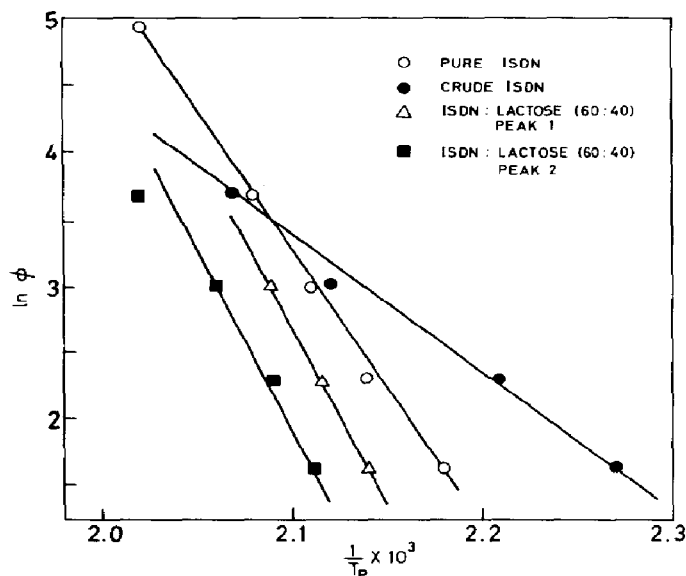


Fig. 6. Ozawa method plot.

TABLE 4

Activation energy values obtained by Ozawa's method

Sample	$E_{act}$ (kJ/mol)
<i>DSC</i>	
Crude ISDN	87.36
Pure ISDN	174.70
ISDN/lactose (60/40)	233.50
<i>TG</i>	
Crude ISDN	68.75
Pure ISDN	158.80

Thermograms were recorded for pure and crude ISDN at four heating rates (5, 10, 20 and 40 K min<sup>-1</sup>). From  $\alpha$ - $t$  curves, the absolute temperatures for the given conversion ( $\alpha=0.5$ ) at different heating rates were calculated. The plot of  $\ln \phi$  vs reciprocal temperature at  $0.5\alpha$  is shown in Fig. 8. The calculated activation energies were 158.8 and 68.7 kJ mol<sup>-1</sup> for pure and crude ISDN, respectively (Table 4). These values are slightly lower than the DSC values.

Weight loss measurement was carried out on four lactose-diluted ISDN samples: (1) ISDN-lactose (80/20); (2) ISDN-lactose (60/40); (3) ISDN-lactose (40/60); and (4) ISDN-lactose (25/75).

The weight loss data is tabulated in Table 5. The samples were heated at fixed heating rate, 10 K min<sup>-1</sup>. The observed weight loss for diluted ISDN was

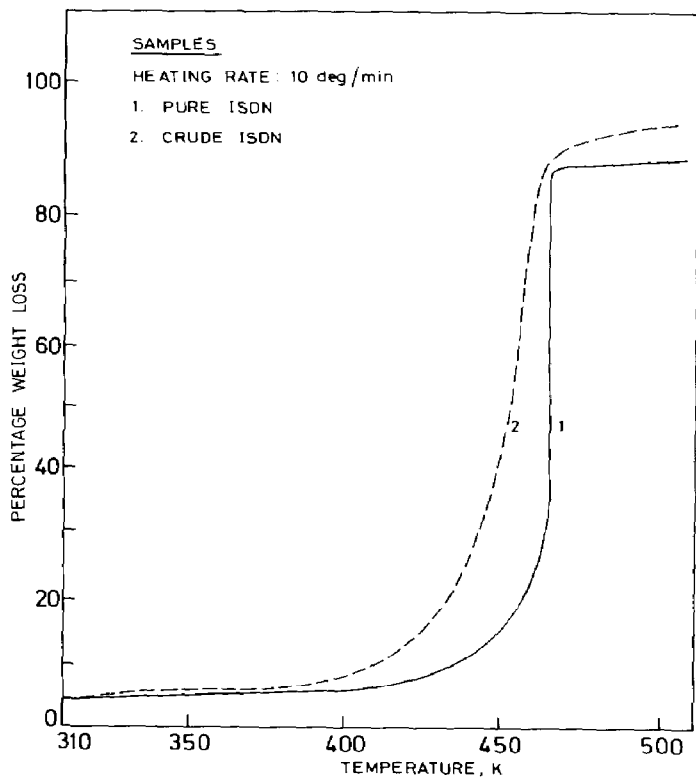


Fig. 7. TG curves of (1) pure, and (2) crude ISDN.

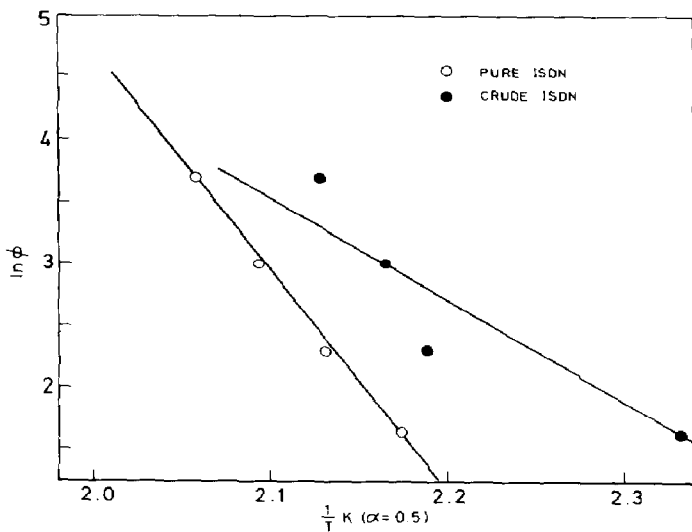


Fig. 8. Ozawa's method for TG analysis.

TABLE 5

Weight loss data TG

Sample		Temperature range (K)	Weight loss (%)	
Pure ISDN		413.0-473.0	90.5	
Crude ISDN		393.0-493.0	84.8	
ISDN/lactose 80/20	Stage I	414.0-434.0	2.0	86.1
	Stage II	434.0-493.0	64.9	
	Stage III	563.0-638.0	20.2	
ISDN/lactose 60/40	Stage I	403.0-430.0	3.1	84.1
	Stage II	430.0-498.0	49.0	
	Stage III	540.0-618.0	32.0	
ISDN/lactose 40/60	Stage I	404.0-434.0	3.9	77.5
	Stage II	424.0-480.0	30.7	
	Stage III	543.0-617.0	42.9	
ISDN/lactose 25/75	Stage I	403.5-428.0	5.6	79.1
	Stage II	428.0-473.0	24.2	
	Stage III	552.0-622.0	49.3	
Pure lactose	Stage I	414.0-447.0	4.3	70.3
	Stage II	512.0-628.0	66.0	

Stage I: Water loss,

Stage II: ISDN decomposition, and

Stage III: lactose decomposition.

in three stages. The first stage loss is mainly due to the loss of lactose water. In the second and third stages, weight loss is due to simultaneous decomposition of ISDN and lactose. The total weight loss was in the range of 70.0-90.0%. As the lactose content increased from 20 to 75%, the percentage total weight loss decreased from 89.1 to 79.1%, while pure lactose showed only 70% loss. As the lactose content increased in ISDN formulation, the loss due to the second stage decreased while third stage weight loss increased according to the lactose percentage. As in the case of DSC analysis, in TG analysis also, the decomposition of ISDN is not really two stage, but the heat absorbing nature of lactose decomposition retards the decomposition rate of ISDN, which is reflected in the rate of weight loss.

### 3.5 Influence of acid on ISDN decomposition

In the manufacturing process of ISDN, isosorbide is nitrated using only nitric acid (99%) or a nitric acid and sulphuric acid mixture. After nitration and

a preliminary water wash, crude ISDN is called acidic ISDN and contains about 0.5–1.0% acid. Subsequently, the acidic ISDN is neutralised with ammonia before subjecting to recrystallisation.

It is known that acidic nitrate esters such as pentaerythritol tetranitrate (PETN) and isosorbide dinitrate (ISDN) are less stable compared to the pure material. Therefore, it is essential to study the thermal stability of acidic ISDN to benefit the manufacturers. We have already noticed low activation energy and low thermal stability for crude ISDN, which is slightly acidic when compared with pure ISDN. The percentage acid in crude ISDN was found to be between 0.5–0.6%.

Further research was carried out on pure ISDN by mixing with known quantities of nitric acid and sulphuric acid separately. Nitric acid showed very little effect on the thermal behaviour of ISDN, whereas the sulphuric acid influence was alarming. The following samples were studied by DSC:

- (1) ISDN + 10% of 10% sulphuric acid,
- (2) ISDN + 20% of 10% sulphuric acid,
- (3) ISDN + 30% of 10% sulphuric acid,
- (4) ISDN + 40% of 10% sulphuric acid,
- (5) ISDN + 50% of 10% sulphuric acid,
- (6) ISDN (pure).

The DSC thermograms are shown in Fig. 9. The thermal stability of ISDN was adversely affected with 10–40% added sulphuric acid, but at 50% sulphuric acid there was no effect on the thermal stability. The onset temperatures for Samples 1, 2, 3, 4, 5 and 6 are 410, 405, 400, 405, 440 and 445 K, respectively. In addition to the melting and decomposition of ISDN, samples with more acid also showed additional small endotherms due to loss of acid water in the temperature range of 380–400 K. This clearly indicates that small percentages of sulphuric acid catalyses the decomposition, but larger percentage of acid acts as a diluent. In fact, some of the acidic ISDN samples (prepared by mixed acid) decomposed while drying at 100°C during TG moisture content determination. Extreme care should be exercised in handling acidic ISDN. It is not advisable to store the acidic material for long periods.

To study the effect of nitric acid on ISDN decomposition, the following samples were prepared by mixing known quantities of nitric acid: (1) ISDN + 10% of 10% nitric acid, (2) ISDN + 30% of 10% nitric acid, and (3) ISDN + 50% of 10% nitric acid.

The onset temperatures for the above samples, 1, 2 and 3, are 438, 439 and 437 K, respectively. These values fall between the onset temperature of pure and crude ISDN (Table 1). Compared to samples mixed with sulphuric acid, the nitric acid influence on ISDN stability is negligible. This may be due to the fact that the nitrate esters on decomposition produce  $\text{NO}_2^+$  species, which will have a common ion effect in the case of nitric acid, whereas sulphuric acid favours decomposition.

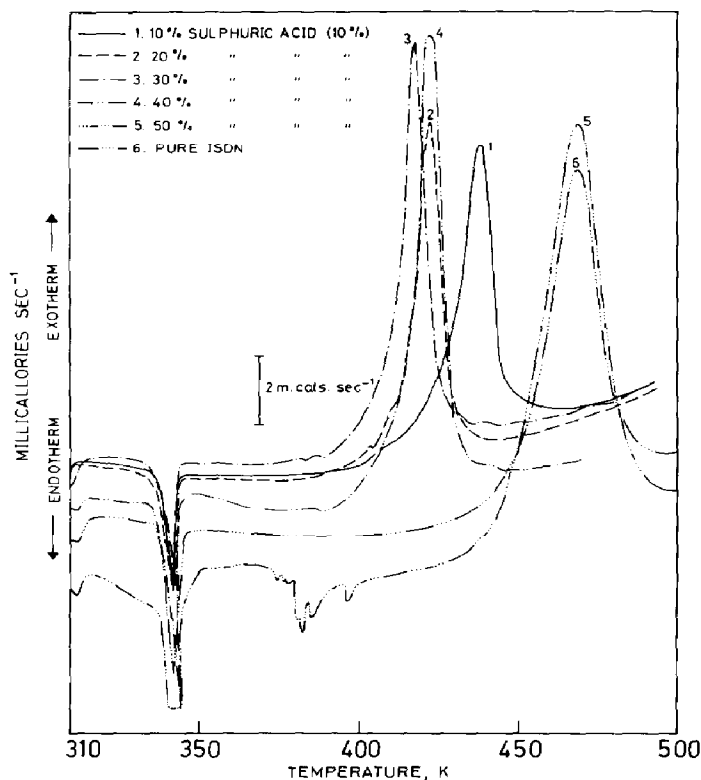
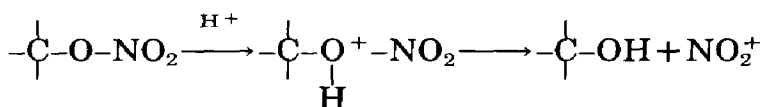


Fig. 9. DSC thermograms showing the influence of sulphuric acid.

### 3.6. Mechanism of decomposition

The activation energy values obtained by TG and DSC study suggest that breakage of the O-N bond in nitrate esters is the rate controlling step, as the activation energy was very close to the O-N bond energy (150-175 kJ mol<sup>-1</sup>). The influence of sulphuric acid on the decomposition of ISDN also supports the above argument. Sulphuric acid, being a strong acid, acts as a strong protonating agent compared with nitric acid, which did not affect ISDN stability to the same extent as sulphuric acid. The influence of sulphuric acid is shown below.



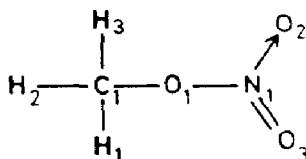
The nitronium ion thus formed is stabilised by sulphuric acid.

In order to understand the effect of protonation on the bond angles, bond length and charge distribution, modified neglect differential overlap (MNDO) calculations were carried out on a model compound, methyl nitrate. The effects of protonation at the alkoxy oxygen O<sub>1</sub> and at the nitro group oxygen O<sub>3</sub> (O<sub>2</sub>)

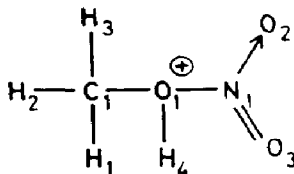
TABLE 6

MNDO calculations

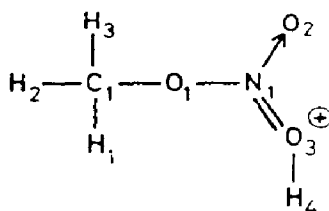
(a) Methyl nitrate



Bond angles (degrees)		Bond lengths (Å)	
O <sub>1</sub> N <sub>1</sub> O <sub>2</sub>	119.92	N <sub>1</sub> -O <sub>2</sub>	1.2091
O <sub>1</sub> N <sub>1</sub> O <sub>3</sub>	114.14	N <sub>1</sub> -O <sub>3</sub>	1.2088
C <sub>1</sub> O <sub>1</sub> N <sub>1</sub>	122.89	O <sub>1</sub> -N <sub>1</sub>	1.3427
H <sub>1</sub> C <sub>1</sub> O <sub>1</sub>	104.50	C <sub>1</sub> -O <sub>1</sub>	1.4202
		H <sub>1</sub> -C <sub>1</sub>	1.1162
H <sub>2</sub> C <sub>1</sub> O <sub>1</sub>	112.50	H <sub>2</sub> -C <sub>1</sub>	1.1144
H <sub>3</sub> C <sub>1</sub> O <sub>1</sub>	112.50	H <sub>3</sub> -C <sub>1</sub>	1.1142

(b) Methyl nitrate protonated at O<sub>1</sub>

Bond angles (degrees)		Bond lengths (Å)	
O <sub>1</sub> N <sub>1</sub> O <sub>2</sub>	91.52	N <sub>1</sub> -O <sub>2</sub>	1.1316
O <sub>1</sub> N <sub>1</sub> O <sub>3</sub>	89.34	N <sub>1</sub> -O <sub>3</sub>	1.1318
C <sub>1</sub> O <sub>1</sub> N <sub>1</sub>	126.14	O <sub>1</sub> -N <sub>1</sub>	2.8418
H <sub>4</sub> O <sub>1</sub> N <sub>1</sub>	122.28	O <sub>1</sub> -H <sub>4</sub>	0.9474
H <sub>1</sub> C <sub>1</sub> O <sub>1</sub>	109.37	C <sub>1</sub> -O <sub>1</sub>	1.4037
		H <sub>1</sub> -C <sub>1</sub>	1.1166
H <sub>2</sub> C <sub>1</sub> O <sub>1</sub>	109.32	H <sub>2</sub> -C <sub>1</sub>	1.1170
H <sub>3</sub> C <sub>1</sub> O <sub>1</sub>	112.87	H <sub>3</sub> -C <sub>1</sub>	1.1130

(c) Methyl nitrate protonated at O<sub>3</sub>

Bond angles (degrees)		Bond lengths (Å)	
O <sub>1</sub> N <sub>1</sub> O <sub>2</sub>	125.36	N <sub>1</sub> -O <sub>2</sub>	1.1820
O <sub>1</sub> N <sub>1</sub> O <sub>3</sub>	115.58	N <sub>1</sub> -O <sub>3</sub>	1.3063
N <sub>1</sub> O <sub>3</sub> H <sub>4</sub>	115.96	O <sub>3</sub> -H <sub>4</sub>	0.9740
C <sub>1</sub> O <sub>1</sub> N <sub>1</sub>	124.21	O <sub>1</sub> -N <sub>1</sub>	1.3086
H <sub>1</sub> C <sub>1</sub> O <sub>1</sub>	102.34	C <sub>1</sub> -O <sub>1</sub>	1.4533
		H <sub>1</sub> -C <sub>1</sub>	1.1121
H <sub>2</sub> C <sub>1</sub> O <sub>1</sub>	111.09	H <sub>2</sub> -C <sub>1</sub>	1.1125
H <sub>3</sub> C <sub>1</sub> O <sub>1</sub>	111.53	H <sub>3</sub> -C <sub>1</sub>	1.1178

TABLE 7

## Detonation properties of ISDN/water mixtures

Shot No.	Composition	Density (g cm <sup>-3</sup> )	VOD (m s <sup>-1</sup> )
1	Crude ISDN + No water	0.82	3921.0
2	Crude ISDN + 5% water	0.87	3849.0
3	Crude ISDN + 7.5% water	0.92	3612.0
4	Crude ISDN + 10.0% water	0.96	Cap failed
5	Crude ISDN + 15% water	1.00	Cap failed
6	Crude ISDN + 20% water	1.04	Cap failed
7	Pure ISDN + 10% water	0.60	3129.0
8	Pure ISDN + 12.5% water	0.81	Cap failed
9	Pure ISDN + 15% water	0.90	Cap failed
10	Pure ISDN + 25% water	0.96	Cap failed
11	Pure ISDN + No water	0.49	4021.0

are shown in Table 6. It appears from the calculations that the most probable site for proton attack is O<sub>1</sub> not O<sub>2</sub> or O<sub>3</sub>. Protonation at O<sub>1</sub> increases the bond length of O<sub>1</sub>-N<sub>1</sub> from 1.3427Å to 2.8418Å. Furthermore O<sub>1</sub> acquires a negative charge, and the whole NO<sub>2</sub> group acquires a positive charge and becomes almost linear. This clearly suggest that protonation at O<sub>1</sub> weakens the O-NO<sub>2</sub> bond so much that little energy is required to break it. The charge distribution explains the presence of some alcohol and nitronium ions in protonated compound. This rationale for methyl nitrate holds for ISDN as well. The decrease



in the activation energy of crude ISDN (which contains about 0.5% sulphuric acid) to half that of pure ISDN is due to the increase of  $-O-NO_2$  bond length the to twice bond length of that in the pure compound.

### *3.7 Detonation properties of ISDN-water mixtures*

ISDN is a cap sensitive explosive in pure form. The detonation properties of ISDN/lactose mixtures were reported earlier [2]. In our present investigation, crude ISDN containing about 2% moisture was diluted with water, packed in 25 mm plastic tubes, and fired with a No. 6 detonator. The results are tabulated in Table 7. Crude ISDN alone showed a detonation velocity of  $3931.0 \text{ m s}^{-1}$ . With up to 7.5% water, it was cap sensitive. With 10% or more water, it was non-cap sensitive. Water was also added to pure ISDN, but it was found that pure ISDN was cap sensitive even with 10% water. These results suggest that ISDN can be made non-explosive by mixing with about 20% water. In its manufacture, ISDN can be handled as a non-explosive by the addition of 20–30% water. However, operations such as crystallisation or drying and mixing with lactose demand the implementation of high explosive rules and regulations as with PETN. Furthermore, though safety is improved by mixing with water, long storage periods with 30% water may affect the quality due to slow hydrolysis.

## **4. Conclusions**

1. Crude or pure ISDN is a high explosive and should be handled carefully.
2. Decomposition enthalpy data clearly shows the dilution effect in ISDN/lactose mixtures.
3. Kinetic data suggests that crude ISDN which contains about 0.5–0.6% acid is more sensitive and less stable compared to pure ISDN.
4. The influence of acidity suggests that the storage of improperly washed ISDN, especially that manufactured using mixed acids, may be unsafe over long periods.
5. Detonation velocity experiments suggest there is enhanced safety when ISDN is mixed with water.

## **Acknowledgements**

The authors wish to thank the management of IDL Chemicals Ltd, for permission to publish this paper. Thanks are due to Mr R. Vedam for his encouragement. Mr P. Sethumadhava Rao is thanked for detonation velocity measurements and Dr V.C. Jyothi Bhasu for MNDO calculations. We also thank Ms Rema Devi for help in preparing the manuscript.

**References**

- 1 Pharmacopoeia of the United States of America, Vol. XIX, U.S. Pharmaceutical Convention Inc., 1942, p. 276.
- 2 B.K. Mohan Murali, V. Ganesan, K. Bhujanga Rao and V. Krishna Mohan, *J. Hazardous Materials*, 3 (1979) 177-182.
- 3 W.A. Seaton, Eli Freedman and D.N. Triweek, CHETAH - The ASTM Chemical Thermodynamic and Energy Release Evaluation Program, ASTM D551, American Society of Testing and Materials, Philadelphia, PA, 1974.
- 4 S.E. Formann, C.J. Carr and J.C. Krantz, *J. Am. Pharm. Assoc.*, 30 (1941) 132.
- 5 T. Ozawa, *Bull. Chem. Soc. Jpn*, 38 (1965) 1881.
- 6 T. Ozawa, *J. Thermal Anal.*, 2 (1970) 301.