(12)

MRL-R-1000

AR-004-445

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-1000

THERMOCHEMISTRY OF NORMAL AND BASIC LEAD STYPHNATES USING DIFFERENTIAL SCANNING CALORIMETRY

M. Maksacheff and D.J. Whelan

Approved for Public Release

DEPARTMENT OF DEFENCE

MATERIALS RESEARCH LABORATORIES

REPORT

MRL-R-1000

THE THERMOCHEMISTRY OF NORMAL AND BASIC LEAD STYPHNATES USING DIFFERENTIAL SCANNING CALORIMETRY

M. Maksacheff and D.J. Whelan

ABSTRACT

The DSC thermogram under non-isothermal conditions from the thermal decomposition of normal lead styphnate, RD 1303M, a component of several primer mixes, is characterised by two peaks. The first is a low temperature endotherm which occurs around 415 K (at a heating rate of 5 K min^{-1}) and corresponds to the loss of water from the crystal lattice, the heat of reaction associated with this process is 67 ± 8 J g^{-1}. The second peak is strongly exothermic with a heat of reaction of 1960 ± 70 J g^{-1} and is associated with an ignition process having an apparent activation energy of 184 ± 11 kJ $mole^{-1}$ and Arrhenius pre-exponential $\log_{10}$ A (s^{-1}) of 14.9 ± 0.5. It is estimated that the T of I of RD 1303M at a heating rate of 5 K min^{-1} occurs between 518 K (the temperature where slow decomposition commences) and 542 K (the onset temperature for rapid decomposition), using the DSC method.

The thermal decomposition of basic lead styphnate, RD 1346, is characterised by a single large exothermic peak, corresponding to a process with an apparent activation energy of 203 ± 12 kJ $mole^{-1}$ and Arrhenius pre-exponential, $\log_{10}$ A (s^{-1}) of 17.7 ± 0.5. The heat of reaction for the complete process is 1170 ± 45 J g^{-1}, and at a heating rate of 5 K min^{-1}, the T of I occurs between 505 K and 525 K (DSC method).

Line shape analysis of the DSC traces from normal lead styphnate suggests its decomposition follows a first-order reaction (n = 1.0 ± 0.1). For basic lead styphnate, the reaction order was determined to be 1.2 ± 0.1.

All DSC experiments were carried out in an inert atmosphere (nitrogen), using aluminium sample pans.

POSTAL ADDRESS: Director, Materials Research Laboratories
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

SECURITY CLASSIFICATION OF THIS PAGE **UNCLASSIFIED**

DOCUMENT CONTROL DATA SHEET

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-R-1000	AR-004-445	Unclassified

TITLE

The thermochemistry of normal and basic lead styphnates using differential scanning calorimetry

AUTHOR(S)

Michael Maksacheff and
Daniel J. Whelan

CORPORATE AUTHOR

Materials Research Laboratories
P.O. Box 50,
Ascot Vale, Victoria 3032

REPORT DATE	TASK NO.	SPONSOR
May, 1986	DST 85/168	DSTO

FILE NO.	REFERENCES	PAGES
G6/4/8-3195	11	18

CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY
Superintendent, MRL
Physical Chemistry Division

SECONDARY DISTRIBUTION

Approved for Public Release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Styphnates; Lead styphnate; Differential scanning calorimetry; Thermochemistry; Thermal decomposition

COSATI GROUPS 1901 0703

ABSTRACT

The DSC thermogram under non-isothermal conditions from the thermal decomposition of normal lead styphnate, RD 1303M, a component of several primer mixes, is characterised by two peaks. The first is a low temperature endotherm which occurs around 415 K at a heating rate of 5 K/min and corresponds to the loss of water from the crystal lattice, the heat of reaction associated with this process is 67 ± 8 J/g. The second peak is strongly exothermic with a heat of reaction of 1960 ± 70 J/g and is associated with an ignition process having an apparent activation energy of 184 ± 11 kJ/mole and Arrhenius pre-exponential $\log_{10}$ A/(s^{-1}) of 14.9 ± 0.5. It is estimated that the T of I of RD 1303M at a heating rate of 5 K/min occurs between 518 K (the temperature where slow decomposition commences) and 542 K (the onset temperature for rapid decomposition), using the DSC method.

The thermal decomposition of basic lead styphnate, RD 1346, is characterised by a single large exothermic peak, corresponding to a process with an apparent activation energy of 203 ± 12 kJ/mole and Arrhenius pre-exponential, $\log_{10}$ A/(s^{-1}) of 17.7 ± 0.5. The heat of reaction for the complete process is 1170 ± 45 J/g, and at a heating rate of 5 K/min, the T of I occurs between 505 K and 525 K (DSC method).

Line shape analysis of the DSC traces from normal lead styphnate suggests its decomposition follows a first-order reaction, (n = 1.0 ± 0.1). For basic lead styphnate, the reaction order was determined to be 1.2 ± 0.1.

All DSC experiments were carried out in an inert atmosphere (nitrogen), using aluminium sample pans.

C O N T E N T S

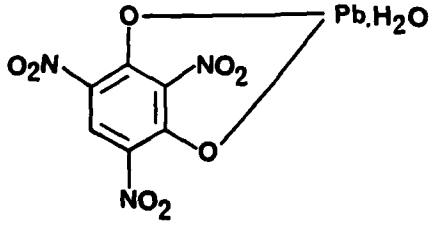
THE THERMOCHEMISTRY OF NORMAL AND BASIC LEAD STYPHNATES USING DIFFERENTIAL SCANNING CALORIMETRY

1. INTRODUCTION

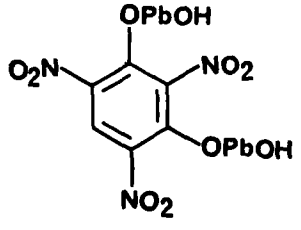
Although considerable kinetic data on a large number of primary explosives already exists [1], there were none available, either from MRL experiments or elsewhere, on either normal lead styphnate (I) (lead trinitoresorcinate), or basic lead styphnate (II). This report seeks to redress this shortcoming and to describe the DSC characteristics and the kinetic parameters associated with the thermal decomposition of these compounds near their temperatures of ignition.

Normal lead styphnate is an initiating explosive, employed mostly as part of a mixture with lead azide, which acts as the detonator charge. Lead styphnate is sensitive to electrostatic ignition and needs to be handled with care, [2]. Its temperature of ignition (T of I) at a heating rate of $5^{o}C\ min^{-1}$ is reported to occur around $257^{o}C$ (uncorr.) (530 K) [3].

Basic lead styphnate is also used in priming compositions, of which one of the best known, NOL 130 [2], consists of 40% basic lead styphnate, 20% lead azide, 2% tetrazene, 15% antimony sulphide and 20% barium nitrate. At a heating rate of $5^{o}C\ min^{-1}$, the T of I of basic lead styphnate is reported to occur at $240^{o}C$ (513 K) [3].



Normal lead styphnate, (I)



Basic lead styphnate, (II)

2. EXPERIMENTAL

2.1 Materials

Both normal lead styphnate and basic lead styphnate were from standard production batches produced at Munitions Filling Factory, St. Marys, N.S.W.

Normal lead styphnate was of the type RD 1303M, mean particle size 31 microns. It exists as a monohydrate.

Basic lead styphnate was of the type RD 1346, of unknown particle size.

2.2 Differential Scanning Calorimetry

Thermochemical measurements were obtained using a Perkin-Elmer DSC-2C Differential Scanning Calorimeter (DSC) operating in the non-isothermal mode, and controlled by a Perkin-Elmer Model 3600 Data Station with appropriate software.

All samples were accurately weighed on a Mettler ME 30 Microanalytical Balance directly into aluminium pans, and lids placed (but not crimped) over the samples [1].

Both compartments of the calorimeter were continuously purged with nitrogen gas throughout the DSC scans, the flow-rate typically being 20-25 ml min^{-1}.

Calibration of the instrument was carried out using the following standards [4],

indium (m.p. 429.8 K, heat of fusion 28.5 J g^{-1})
tin (m.p. 505.1 K)
lead (m.p. 600.7 K)

It was found that, from measurement to measurement, variations in recorded temperature were of the order of ca. ± 0.7 K and in recorded heats of reaction were ca. ± 2.5 per cent.

3. RESULTS

3.1 Normal lead styphnate

The DSC trace for normal lead styphnate over the temperature range from 320 K to 780 K consists of a small broad pre-ignition endotherm and a large, sharp exotherm (Fig. 1). The "peak temperature" (or "the temperature

at which the rate of dissipation/uptake of heat is greatest") and the "onset temperature" were dependent on the rate of heating (Table 1).

At a heating rate of 5 K min^{-1}, the heating rate corresponding to the conventional "temperature of ignition" experiment [3], it can be observed (Fig. 2) from the DSC trace that significant thermal decomposition commences near 518 K; the extrapolated onset temperature corresponding to thermal ignition, occurs at 542 K, and the reaction has a maximum heat output at 560 K. These results compare well with the T of I, determined on the ERDE-designed instrument at MRL [3], of 530 K.

The area under the DSC trace measures the heat of reaction of the process under investigation. For normal lead styphnate, the average heat of reaction value was determined to be 1960 ± 70 J g^{-1}, (470 ± 17 cal g^{-1}).

As mentioned previously, the DSC trace of normal lead styphnate exhibited a pre-ignition endotherm; at a heating rate of 5 K min^{-1}, this reaction process commenced at 415 K, the extrapolated onset temperature occurred at 416 K and the sample has a maximum heat uptake at 425 K (Fig. 2). From a consideration of all experimental scans, the heat of reaction for this endothermic process was determined to be 67 ± 8 J g^{-1} (16.0 ± 1.9 cal g^{-1}).

A weight loss experiment was carried out to determine the nature of this endothermic reaction and it was found that an average "weight loss" value of 3.7 ± 0.3% was observed from triplicate samples heated from room temperature to 480 K in the DSC apparatus. This weight loss corresponds to a loss of one molecule of H_2O from each molecule of normal lead styphnate (calculated weight loss 3.84 per cent).

The kinetic parameters of the thermal decomposition of normal lead styphnate, namely, the activation energy, E*, the apparent first-order Arrhenius pre-exponential term, A, and the reaction order, n, were determined from Kissinger's treatment of the DSC data [5,6], and the line shape of the DSC curves, as described by Kissinger [6], and amplifieid by Hauser and Field [7], and by Dollimore and co-workers [8].

In his approach to the calculation of the activation energy, Kissinger established that there is a relationship between the peak temperature (T_m) and the heating rate of an apparent first order reaction, and this relationship can be best summarized by the equation,

$$A \exp(-E^*/R\,T_m) = \frac{E^*}{R\,T_m^2} \cdot \frac{dT}{dt} \qquad (1)$$

where R is the gas constant, $\frac{dT}{dt}$ is the time rate of heating the sample. This equation can be rewritten as

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln\left(\frac{A\ R}{E^*}\right) - \frac{E^*}{R} \cdot \frac{1}{T_m} \qquad (2)$$

where $\Phi = dT/dt$, from which a plot of $\ln (\Phi/T_m^2)$ vs $1/T_m$ is a straight line of slope, $-E^*/R$. Kissinger showed that even for an nth order reaction, reasonable approximations can be made which reduce the kinetics to a form where this equation can apply, regardless of reaction order; the pre-exponential term, A, has the dimensions $(\text{time})^{-1}$, and can be regarded as a pseudo first-order constant. When the data in Table 1 is plotted out according to equation (2), the following parameters were obtained for the thermal decomposition of normal lead styphnate near its temperature of ignition:

$E^* = 183.5\ (\pm\ 10.8)$ kJ mole^{-1},
$\log_{10} A(s^{-1}) = 14.86\ (\pm\ 0.45)$,
correlation coefficient = 0.9987, (4 points).

Kissinger also showed that the order of the reaction under investigation can be determined by the shape of the DSC trace. This approach is best summarized by equation 3,

$$n = 1.26 \left(\frac{a}{b}\right)^{1/2} \qquad (3)$$

where n is the order of the reaction, and a and b are displacement measurements defined by the tangents to the point of maximum heat output in the DSC trace (Fig. 5).

Using this analysis, n was determined to be 1.0 ± 0.1, based on the traces from experiments at the heating rates of 20 and 10 K min^{-1}.

3.2 Basic Lead Styphnate

The DSC trace for basic lead styphnate over the temperature range from 320 K to 780 K consists solely of a large sharp exotherm (Fig. 3), the peak temperature and the onset temperature for the decomposition reaction being dependent on heating rate (Table 2).

At a heating rate of 5 K min^{-1}, it can be seen (Fig. 4) that thermal decomposition commences at 505 K, the onset temperature occurs at 525 K, and the sample has a maximum heat output at 533 K. This compares well with the conventional T of I measurement on the ERDE-designed instrument at MRL [3], of 513 K.

The mean value of the heat of reaction for basic lead styphnate from all experiments was determined to be 1170 ± 45 J g^{-1} (280 ± 11 cal g^{-1}) (Table 2). The following kinetic parameters were obtained from the Kissinger plot, using the data of Table 2:

$E^* = 202.5\ (\pm\ 11.9)$ kJ mole^{-1},
$\log_{10} A(s^{-1}) = 17.68\ (\pm\ 0.53)$,
correlation coefficient = 0.9991 (4 points).

Line shape analysis of the DSC traces at the heating rates of 20 and 10 K min^{-1} gave a reaction order, n, of 1.2 ± 0.1.

4. DISCUSSION

In Table 4, the results for normal lead styphnate (I) and basic lead styphnate (II) are presented alongside those for a selection of primary explosives [1,9]. These results show that:

(i) the heat of reaction associated with the thermal decomposition of normal lead styphnate, 1960 J g^{-1}, is significantly higher than that of basic lead styphnate, 1170 J g^{-1}, reflecting the greater number of reactive centres (- NO_2, $\geq$CH, less Pb, etc.) per unit mass in the normal salt.

(ii) the heat output for these two salts is comparable with that of 5-nitro-2-picryl-tetrazole, 1340 J g^{-1}, but much larger than that of tetrazene, 670 J g^{-1} [9]. However, a caveat should be heeded in using these data to compare the performance of these compounds as primary explosives as power output is probably more important than actual energy output.

How do these results for lead styphnate compare to those reported by Hailes and Garner over fifty years ago [10,11]? Hailes used classical manometric techniques to follow the rate of thermal decomposition of single crystals (0.5 ~ 5 mg) of lead styphnate around the temperature of ignition (513 K) over the range 498 K to 516 K. He suggested that thermal decomposition of single crystals of lead styphnate, following loss of its water of crystallization, proceeds by a two-step process, the first being a true thermal decomposition, whose rate-determining step characterised by an energy of activation of 196 kJ $mole^{-1}$; this is a value very close to that determined in the present DSC study, 184 kJ $mole^{-1}$.

According to Hailes, if the reaction proceeds to detonation or very rapid burn, the second process takes over, obeying first-order kinetics with an activation energy of ca. 163 kJ $mole^{-1}$. He found that this latter reaction did not always occur under the conditions of his experiments and explained his results in terms of the effect on the propagation of reaction of crystals size, crystal imperfections (lattice defects, grain boundaries, cracks in the cyrstals, agglomeration of crystallites, diffusion of reaction products, etc.) and the amount of material present. The larger the sample, the more likely the decomposition of the sample would proceed to the detonation phase of the reaction.

In the present study, the samples of lead styphnate and basic lead styphnate were relatively small masses of finely powdered material. One therefore supposes that the reaction observed here only paralleled that in the first step of Hailes' reaction pathway.

5. REFERENCES

1. D.J. Whelan, R.J. Spear and R.W. Read, "The Thermal Decomposition of Some Primary Explosives as studied by DSC", Thermochim Acta, 80 (1984) 149-163.

2. B.T. Fedoroff and O.E. Sheffield (Editors) "Encyclopedia of Explosives and Related Items", Picatinny Arsenal (Dover), New Jersey, U.S.A. Technical Report 2700 (a) 1972, Vol. 5 D1277-1287.

3. G. Bocksteiner (Explosives Materials Group, MRL) (1985) unpublished results on the temperature of ignition of primary explosives.

4. Perkin-Elmer, "Model DSC-2C Differential Scanning Calorimeter Instruction Manual", 1979, Section 3E.

5. H.E. Kissinger, "Variation of Peak Temperature with Heating Rate in Differential Thermal Analysis", J. Res. Natl. bur. Stds., 57 (1956) 217-221.

6. H.E. Kissinger, "Reaction Kinetics in Differential Thermal Analysis", Anal. Chem., 29 (1957) 1702-1706.

7. H.M. Hauser and J.E. Field, "New Method for TG and DSC Data Analysis", Thermochim Acta, 27 (1978) 1-8.

8. M.S. Fatemi, R. Whitehead, D. Price and D. Dollimore. "Determination of Activation Energy from the Maximum Rate of Reaction Points obtained from Non-isothermal Experiments", Thermochim Acta, 73 (1984) 437-440.

9. R.J. Spear and M. Maksacheff, "The Relationship between Ignition Temperature and Thermal Stability for Selected Primary Explosives", (1986) to be submitted for publication.

10. H.R. Hailes and W.E. Garner, quoted by W.E. Garner, "The Chemistry of the Solid State" (Editor, W.E. Garner), Butterworth (London) 1955, Chapter 9, "The Kinetics of the Exothermic Solid Reactions", pp 232-245.

11. H.R. Hailes, "The Thermal Decomposition of Lead Styphnate" Trans. Farad. Soc., 29, (1933) 544-549.

TABLE 1

Experimental Features of the DSC Traces from Normal Lead Styphnate

Heating Rate: 2.5K/min
Mass of Samples: 0.525 mg, 0.510 mg

	Endotherm	Exotherm
Tonset (K)	405	533
Tmax (K)	414	552
Heat of Reaction (J/g)	65	1890

Heating Rate: 5K/min
Mass of Samples: 0.486 mg, 0.508 mg

	Endotherm	Exotherm
Tonset (K)	416	542
Tmax (K)	425	560
Heat of Reaction (J/g)	59	1930

Heating Rate: 10K/min
Mass of Samples: 0.469 mg, 0.465 mg

	Endotherm	Exotherm
Tonset (K)	423	554
Tmax (K)	434	571
Heat of Reaction (J/g)	75	2010

Heating Rate: 20K/min
Mass of Samples: 0.463 mg, 0.447 mg

	Endotherm	Exotherm
Tonset (K)	436	564
Tmax (K)	447	580
Heat of Reaction (J/g)	69	2010

TABLE 2

Experimental Features of the DSC Traces from Basic Lead Styphnate

Heating Rate:	2.5K/min
Mass of Samples:	0.520 mg, 0.543 mg
	Exotherm
Tonset (K)	518
Tmax (K)	525
Heat of Reaction (J/g)	1110

Heating Rate:	5K/min
Mass of Samples:	0.488 mg, 0.529 mg
	Exotherm
Tonset (K)	525
Tmax (K)	533
Heat of Reaction (J/g)	1200

Heating Rate:	10K/min
Mass of Samples:	0.474 mg, 0.501 mg
	Exotherm
Tonset (K)	533
Tmax (K)	541
Heat of Reaction (J/g)	1180

Heating Rate:	20K/min
Mass of Samples:	0.486 mg, 0.496 mg
	Exotherm
Tonset (K)	542
Tmax (K)	549
Heat of Reaction (J/s)	1190

TABLE 3

Arrhenius Parameters for Thermal Decomposition Reaction as studied by DSC (based on Kissinger's Method [5,6])

Compound	Normal Lead Styphnate	Basic Lead Styphnate
E* (kJ/mole)	183 5 (±10.8)	202.5 (±11.9)
log A (s^{-1})	14.86 (±0.45)	17.68 (±0.53)
Average Heat of Reaction (J/g)	1960 ± 70	1170 ± 45
Kissinger Plot No. of Coords.	4	4
Correlation Coefficient	0.999	0.999

TABLE 4

Kinetic and Thermochemical Data associated with the Thermal Decomposition of Various Primary Explosives under Ignition Conditions, under Nitrogen [1,3,9]

Compound	T of I (K)	E* (kJ/mole)	$\log_{10}$ A (s^{-1})	Heat of Reaction (J/g)
Tetrazene	409	163	18.7	670
5-Nitro-2-Picryl-Tetrazole	429	269	30.2	1340
Mercuric-bis-Fulminate	431	117	11.5	--
Basic Lead Styphnate	513	203	17.7	1170
Normal Lead Styphnate	530	184	14.9	1960
Lead Azide	589	197	15.3	--

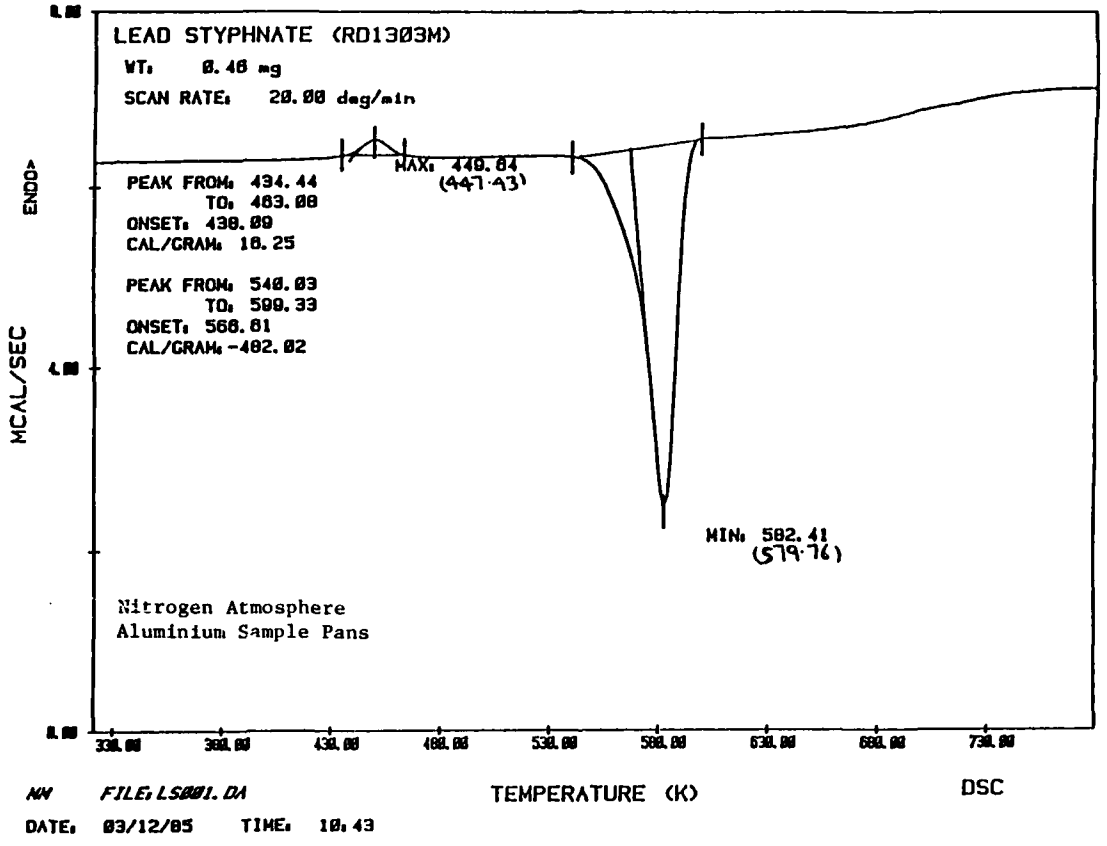


FIGURE 1 Non-isothermal DSC trace of lead styphnate from 320K to 770K at a heating rate of 20K/min.

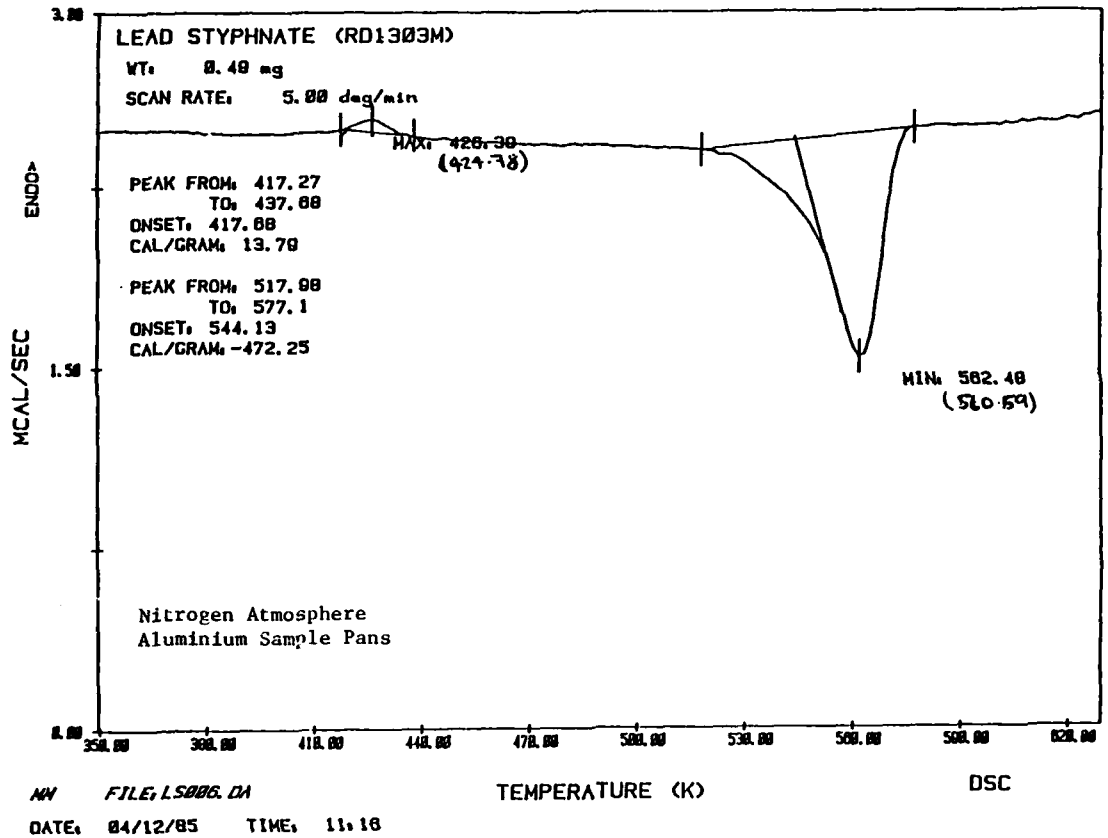


FIGURE 2 Non-isothermal DSC trace of lead styphnate from 350K to 630K at a heating rate of 5K/min.

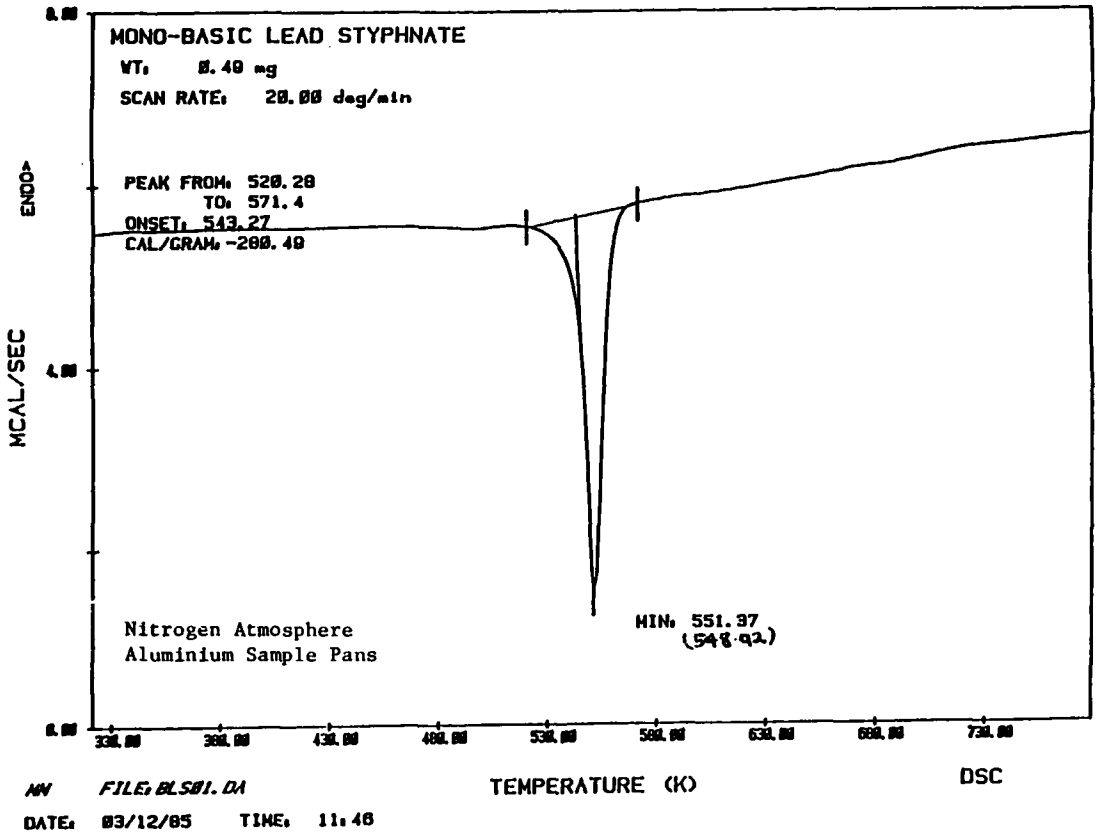


FIGURE 3 Non-isothermal DSC trace of basic lead styphnate from 320K to 770K at a heating rate of 20K/min.

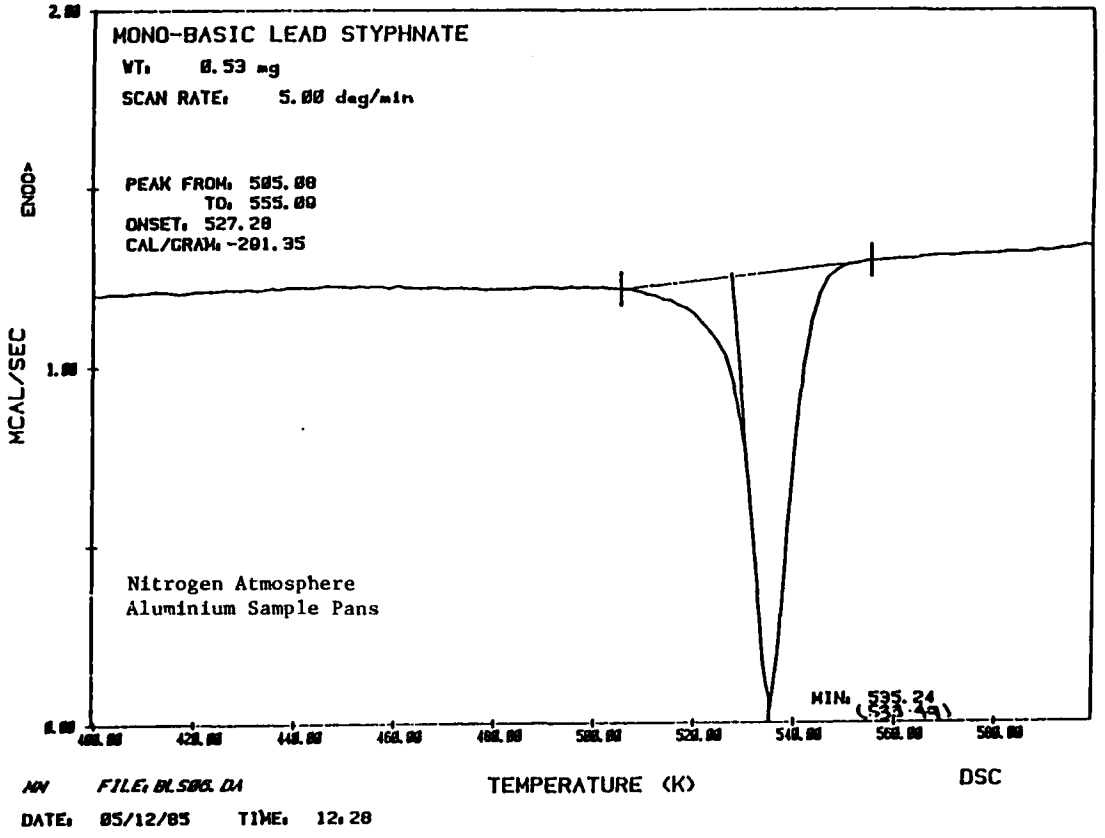


FIGURE 4 Non-isothermal DSC trace of basic lead styphnate from 400K to 600K at a heating rate of 5K/min.

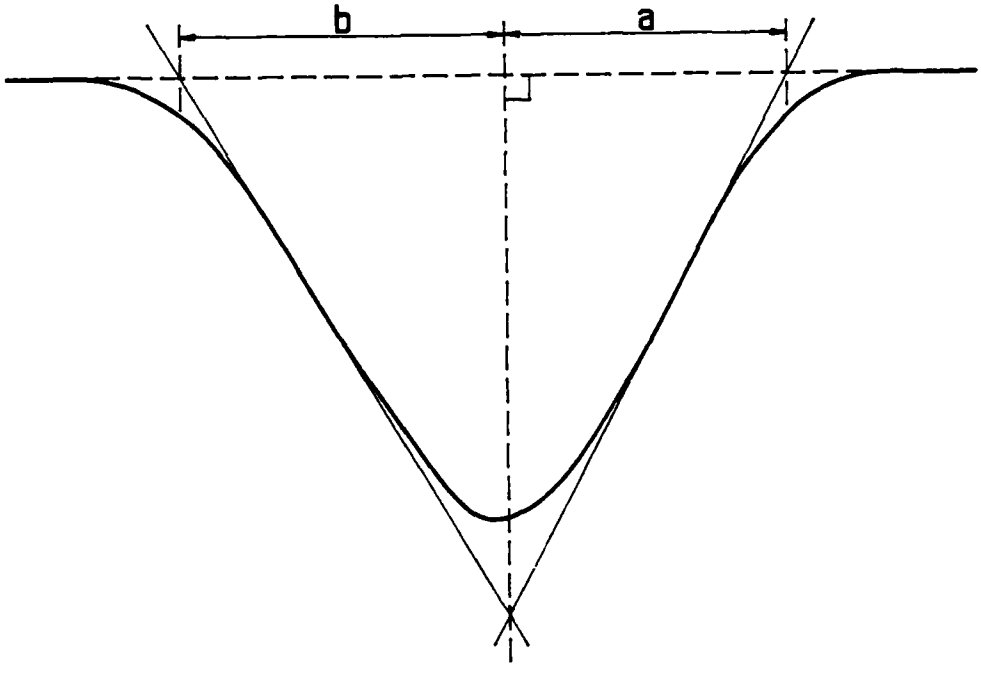


FIGURE 5 For an idealised DSC trace, the shape index is related to the order of the reaction under investigation. It is defined as the absolute value of the ratio of the slopes of the tangents to the curve at the inflection points of the DSC trace.

This can be summarised by the equation:

$$\text{shape index} = s = \frac{a}{b}$$

hence

$$\text{order} = n = 1.26\ s^{1/2}$$