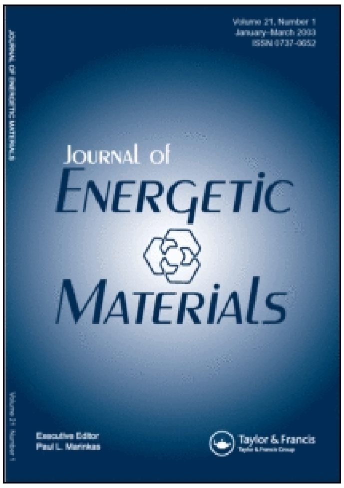

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# The thermal decomposition of basic lead styphnate RD 1349 at its ignition temperature

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# THE THERMAL DECOMPOSITION OF BASIC LEAD STYPHNATE RD 1349 AT ITS IGNITION TEMPERATURE

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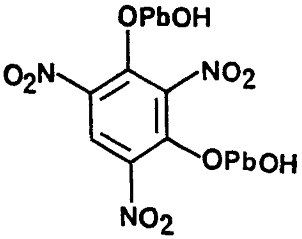
## ABSTRACT

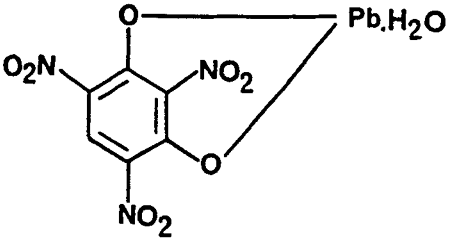
Basic lead styphnate RD 1349 forms the primary explosive component of several high temperature fuzehead formulations and percussion primers. A study of its thermal decomposition under controlled conditions near its ignition temperature (521-525 K) shows that it decomposes very rapidly, following a second order autocatalytic rate law. The kinetics of this reaction are initially controlled by the "nucleation of reactive molecules" occurring on the crystal surfaces or glide planes, by the growth of these nuclei as the reaction proceeds and, in the rate determining step, by their subsequent reaction in the bulk of the material. The rate determining step in this reaction follows Arrhenius kinetics with an activation energy of 197 kJ $mol^{-1}$ and pre-exponential $\log_{10} A\ (s^{-1}) = 17.9$.

## INTRODUCTION

There have been several papers on the isothermal decomposition of primary explosives [1-5] including lead styphnate [4] and barium styphnate [5] but no similar study has been reported on basic lead styphnate, (1). This is surprising as basic lead styphnate



(1)



(2)

is widely used not only as one of the primary explosive components of the primer mix NOL 130 but also as the initiating increment in several high temperature fuzehead formulations [6]. It is also considered preferable to normal lead styphnate (2) in those stores which may be subjected to high temperatures (in excess of ca. 130°C) where it is possible that normal lead styphnate may lose its water of crystallisation on long term exposure.

To redress this omission, the present study was undertaken using the techniques of isothermal differential scanning calorimetry [7] to follow the kinetics of the exothermic reaction associated with the thermal decomposition of basic lead styphnate over the temperature range 520-540 K where basic lead styphnate undergoes controlled ignition [8].

## EXPERIMENTAL

### Materials

Basic lead styphnate exists in at least two polymorphic forms [9]. The sample provided for this study was the beta polymorph, RD 1349, prepared at these laboratories by Mr P. Elischer following a standard procedure [6]; it consisted of fine, needle-like crystals, whose temperature of ignition occurred at 523 K (250$^{o}$C) at a heating rate of 5 K min$^{-1}$ (lit. 519-524 K [6,9]).

### Differential Scanning Calorimetry

Thermochemical measurements were obtained using a Perkin-Elmer DSC-2C Differential Scanning Calorimeter controlled by a Perkin-Elmer Model 3600 Data Station with appropriate software.

All samples were accurately weighed on a Mettler ME30 Microanalytical Balance directly into aluminium sample pans and lids placed (but not crimped) over the samples [8].

The sample and reference compartments of the calorimeter were continuously purged with nitrogen gas throughout the DSC scans, the nitrogen flow rate typically being 20-25 ml min$^{-1}$, nominally at atmospheric pressure.

Isothermal DSC traces were carried out following the procedure described in the Perkin Elmer Software Package, "ISOTHERMAL", using thermally-balanced sample and reference compartments. From non-isothermal DSC traces (such as Fig. 1) it was apparent that basic lead styphnate was quite stable at temperatures below 475 K and that slow but obvious decomposition appeared to occur only above ca 500 K.

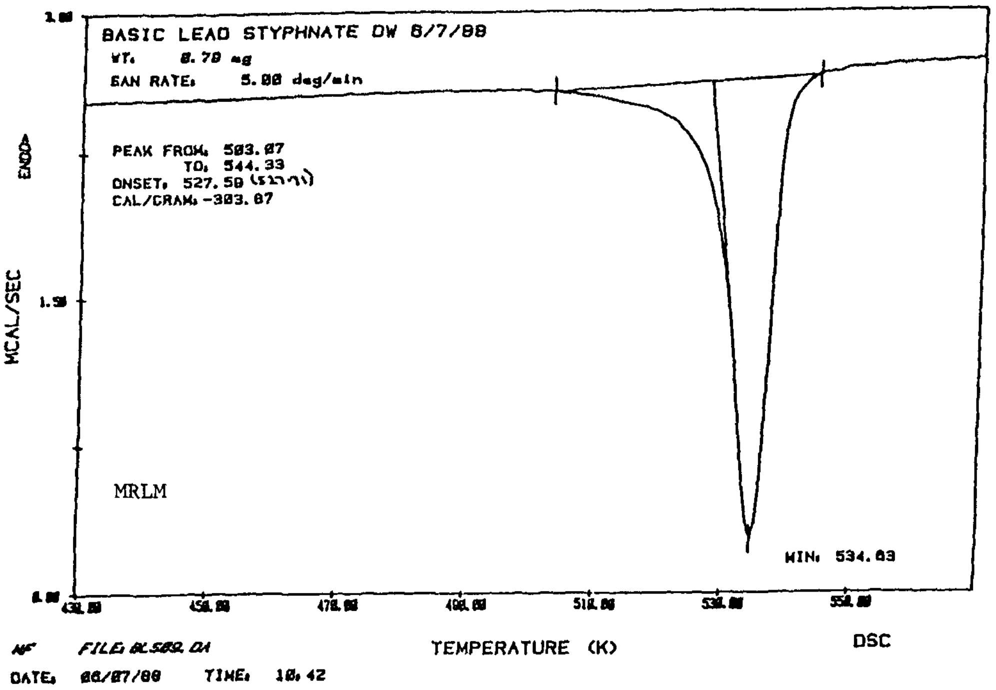


FIGURE 1. Non-isothermal DSC trace of basic lead styphnate from 400 K to 600 K at a heating rate of 5 K $min^{-1}$ (Al pans, $N_2$ atmos.).

Preliminary experiments indicated that the progress of the reaction could be conveniently followed by DSC studies over the "nominal" temperature range 520–540 K and the measured heat output was of the order of 1320 ± 45 J $g^{-1}$, suggesting that sample masses of ca. 0.5 mg would be appropriate for studying this reaction.

In most experiments, the sample in an aluminium sample pan was loaded into the sample compartment of the calorimeter, which had been previously heated to a temperature of 80 K below the temperature chosen for the study. The sample was allowed to equilibrate at this temperature (ca. two minutes) and then the temperature of the calorimeter raised rapidly (at 80 K $min^{-1}$) to the final temperature. The progress of the reaction was followed by observing the change in output of heat (dQ/dt) with time (t), the actual heat output being corrected for that associated with "blank runs" at the same temperature.

The DSC trace from the isothermal decomposition of basic lead styphnate at 528.6 K (corr.) is given in Fig. 2. It is typical of the traces obtained at other temperatures.

## RESULTS

### (a) Thermal Decomposition

The first step in an experimental study of a solid state reaction is to determine the relationship between the extent of reaction or fractional decomposition of a reactant, $\alpha$, and the reaction time, t. Analysis of the data presented in Fig. 2 yields the sigmoidal $\alpha$-t plot given in Fig. 3, not atypical of $\alpha$-t plots observed from solid state reactions involving the formation, interaction and dissipation of reactive nuclei [10–12].

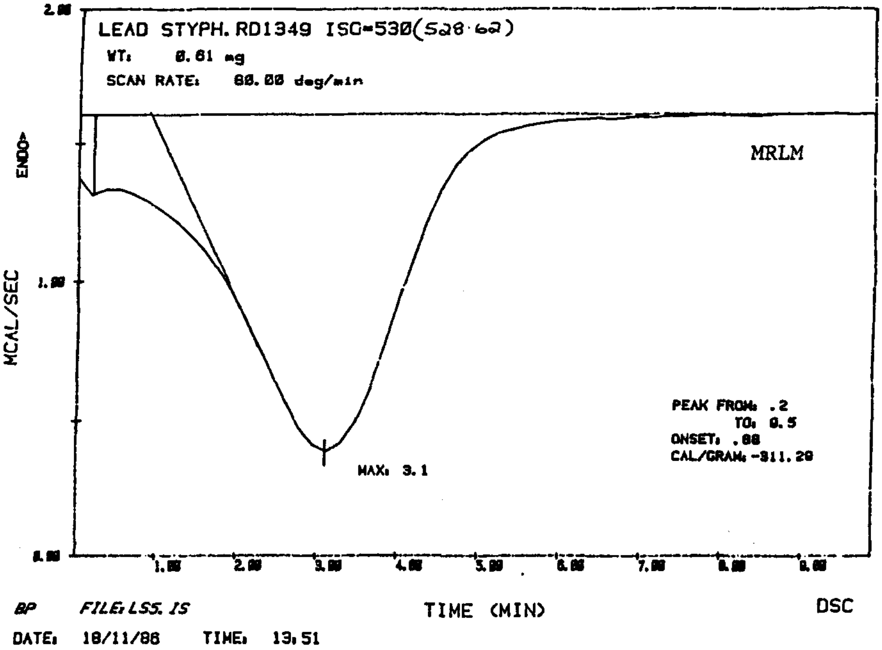


FIGURE 2. Isothermal DSC trace of basic lead styphnate RD 1349 at 528.6 K (Al pans, $N_2$ atmos.).

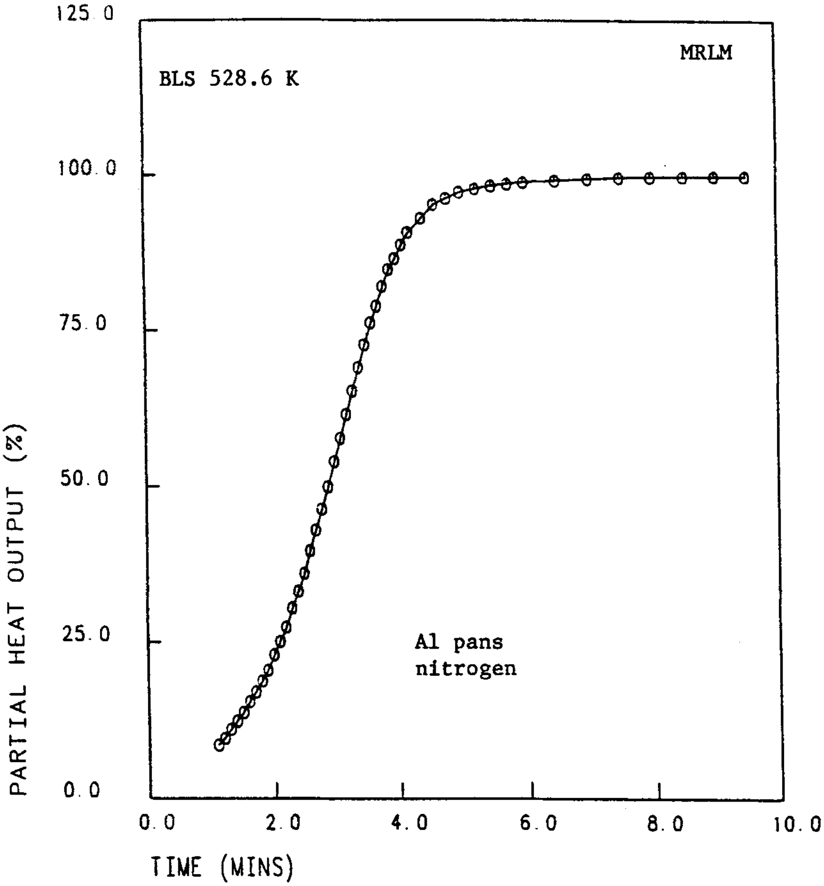


FIGURE 3. Heat output (%) from basic lead styphnate RD 1349 at 528.6 K.

Three major stages have been identified [10-12] in reactions such as this where

$$A_{(solid)} \rightarrow B_{(solid)} + C_{(gas)} \qquad \text{(Eq 1)}$$

These are

(i) a prenucleation process, often of relatively short duration, accompanied by the formation of a large number of reaction centres. This is often called the "quiescent period of the reaction" where very little decomposition occurs.

(ii) a major reaction domain where the decomposition proceeds rapidly according to one or several rate laws defined by the spatial distribution of the nuclei in the reactant matrix, and

(iii) a reaction domain where the reactant nuclei dissipate or coalesce with product nuclei.

Let us consider the DSC thermogram of basic lead styphnate at 528.6 K (Fig. 2) and its corresponding $\alpha$-t plot (Fig. 3).

If one compares the $\alpha$-t traces described by Harrison [12], Garner [11] or Jacobs and Tompkins [10] with those obtained in the present work, it is immediately apparent that

(i) the reaction under investigation here follows a pattern similar to that described above and is already in the second stage of this sequence ("the acceleration stage") after <u>ca.</u> 1.0 min at 528.6 K, and

(ii) the rate of reaction (as measured by dQ/dt or $d\alpha/dt$) is a maximum when the reaction coordinate $\alpha$ is (approx.) 0.5 (actually $0.5_5$).

This latter observation suggests that the thermal decomposition of basic lead styphnate may be governed by a rate law such as the Prout-Tompkins relationship [13,14],

$$\frac{d\alpha}{dt} = k_2 \alpha (1 - \alpha) \qquad \text{(Eq 2)}$$

which has a maximum value at $\alpha = 0.5$, from which $k_2 = 4 \ (d\alpha/dt)_{max}$, and which gives rise to a sigmoidal $\alpha$-t profile.

Integration of this equation leads to

$$k_2 t = \ln\left(\frac{\alpha}{1-\alpha}\right) + \text{Constant} \qquad \text{(Eq 3)}$$

A plot of $\ln(\alpha/1-\alpha)$ vs. t using the data derived from Figs. 2 and 3 followed a straight line relationship (coefficient of determination = 0.993) for that part of the reaction between $\alpha = 0.25$ and $\alpha = 0.75$, with a gradient corresponding to a value of $k_2$ of $1.45_9$ $\text{min}^{-1}$. This suggests that, at least in this range, basic lead styphnate is decomposing according to Eq. 1 by a rate law, the kinetics of which satisfy Eq. 2 and Eq. 3.

Outside the range $0.75 > \alpha > 0.25$, there is an apparent departure from Prout-Tompkins kinetics. At $\alpha < 0.25$, this departure may be artificial because any error in $\alpha$ will cause significant errors in $(\alpha/1-\alpha)$ and therefore in $\ln(\alpha/1-\alpha)$; at $\alpha > 0.75$, however, this departure is probably real as "order" or "coherence" within the crystalline matrix is grossly distorted by product molecules.

The experimental data was analysed in various other ways [15] but the Prout-Tompkins treatment gave the best results.

(b) Kinetic Parameters

As mentioned earlier, the pattern of the thermal decomposition of basic lead styphnate at 528.6 K is typical of that followed at other temperatures in the range 520-540 K. At these temperatures, the major part of the thermal decomposition proceeds via a rate law described by Eq. 3 from which appropriate rate constants were determined (Table 1).

TABLE 1

The Thermal Decomposition of Basic Lead Styphnate RD 1349 : Prout Tompkins Kinetics (520 - 540 K)

| **Temperature $(K)_{corr}$** | **Rate Constant, $k_2$ $(min^{-1})$** | **Range where Prout-Tompkins kinetics followed:** |
|---|---|---|
| 519.4 | 0.647 | $0.75 > \alpha > 0.25$ |
| 519.4 | 0.738 | $0.75 > \alpha > 0.25$ |
| 520 | 0.684 | $0.75 > \alpha > 0.35$ |
| 520 | 0.718 | $0.75 > \alpha > 0.25$ |
| 528.6 | 1.459 | $0.75 > \alpha > 0.25$ |
| 528.6 | 1.383 | $0.75 > \alpha > 0.25$ |
| 530 | 1.570 | $0.85 > \alpha > 0.20$ |
| 530 | 1.730 | $0.85 > \alpha > 0.20$ |
| 530 | 1.480 | $0.85 > \alpha > 0.20$ |
| 538.8 | 3.507 | $0.85 > \alpha >$ ?<br>very fast reaction |
| 540.0 | 4.072 | $0.85 > \alpha >$ ?<br>very fast reaction |

Arrhenius Plot

$E^* = 197$ kJ mol$^{-1}$

$\log_{10} A\ (s^{-1}) = 17.89$

Coefficient of Determination = 0.990

These follow an Arrhenius law quite well, a linear least squares plot yielding

$$E^{*} = 197 \text{ kJ mol}^{-1}$$

$$\log_{10} A\ (\text{s}^{-1}) = 17.8_{9}$$

(Coefficient of determination = $0.99_{0}$).

These results compare quite well with those reported by Maksacheff and Whelan [8] from DSC studies of the non-isothermal decomposition of basic lead styphnate; in that study, the DSC traces were analysed on the basis of the simplifying assumption that the temperature at which maximum heat output occurred depends on the heating rate and the activation energy of the reaction being studied.

### (c) Reaction Products

Experiments indicated that the isothermal and non-isothermal decomposition of basic lead styphnate (RD 1349) over various temperatures between 520 K and 570 K results in a mass loss of 19.4 ± 0.4 per cent (av. of 10 experiments) and is independent of temperature over this range.

Unfortunately, the authors did not have facilities at their disposal necessary to monitor and determine the nature of the gaseous products given off in the course of this reaction. However, there are relevant results available from the Cambridge group [16, 17] on the application of time-resolved quadrupole mass spectrometry on two related compounds, lead styphnate and lead (II) dinitroresorcinate.

It appears that from the "low energy, slow" decomposition of lead styphnate (monohydrate), the main gaseous products consisted of $H_2O$ (18 a.m.u.), $N_2$ and/or CO (28 a.m.u.), NO (30 a.m.u.) and $CO_2$ (44 a.m.u.), with lesser amounts of H,NO (31 a.m.u.), HCNO (43 a.m.u.) and $NO_2$ (46 a.m.u.) being detected [16].

From lead (II) dinitroresorcinate, the products consisted of (approx.) 1 $H_2O$, 1 $N_2$ and/or CO and 1-1.5 $CO_2$ [17].

One supposes that similar products would be obtained from more conventional thermal decomposition studies, as described herein, and - if this is so - one expects similar products from basic lead styphnate (BLS). If the overall reaction is described by the equation

$$\text{BLS} \rightarrow \text{Solids} + 1.5\,H_2O + N_2 + NO_2 + 0.5\,(CO + CO_2)$$

the gaseous products would account for a mass loss of 19.8 per cent from the system (found: 19.4 ± 0.4 per cent).

## DISCUSSION

In a study such as this, three questions immediately arise.

(i) How do these results compare with those from other primary explosives?

(ii) What is the significance of the rate law governing the thermal decomposition of basic lead styphnate?

(iii) What are the implications of these results in an initiated explosion?

From the limited data presented in Table 2 drawn from various sources [1-4, 16-20], it can be seen that the activation energy for the thermal decomposition of basic lead styphnate is greater than that of other primary explosives but its heat output per unit mass is generally much less. These thermochemical parameters suggest that there may be an inbuilt margin of safety inherent in basic lead styphnate not present in some of the other primary explosives and further suggest criteria based on DSC/kinetic studies which may be useful in evaluating possible replacement materials for basic lead styphnate in time to come.

TABLE 2

Kinetic and Thermochemical Data associated with the Thermal Decomposition of Various Primary Explosives under Ignition Conditions in an Inert Atmosphere

| **E*** **($kJ\ mol^{-1}$)** | **$log_{10}A$** **($s^{-1}$)** | **Heat of Reaction** **($J\ g^{-1}$)** | **Reference/Comments** |
|---|---|---|---|
| Basic Lead Styphnate (473-503 K) | | | |
| 198 | 17.9 | 1320 | This work |
| Lead Styphnate $H_2O$ (468-505 K) | | | |
| 138, 150 | | 1960 | [18, 4, 3] |
| $\beta$- Lead Azide (480-540 K) | | | |
| 123 ± 12 | - | | [19] Fracture |
| 160 | | 1650 | [1, 20] Manometric |
| Mercuric Fulminate (380-400 K) | | | 2 Steps |
| 79 | - | | Quiescent reaction |
| 113 | | | Acceleratory reaction |
| 125-135 | 14.9 | 1520 | [1, 2] |
| Mercuric 5-Nitrotetrazolate (440-450 K) | | | 2 Stages [1] |
| 150 | 15.3 | 2070 | 1st Stage |
| 137 | 12.3 | | 2nd Stage |
| Silver (I) 5-Nitrotetrazolate (485-525 K) | | | 2 Stages [1] |
| 246 | 22.7 | 1940 | 1st Stage |
| 166 | 14.6 | | 2nd Stage |
| Lead (II), 2,4-Dinitroresorcinate (493-523 K) | | | |
| 173 | | 960 | [17] |

As to the significance of the reaction kinetics, much has been written [10-14]. In its original form, the Prout-Tompkins equation was derived theoretically on the basis of a self-terminating branching chain mechanism. In the natural order of the solid state, the most reactive sites are those of maximum potential energy where the reactant molecule is located at a surface defect, glide plane or crack. As reaction proceeds, product molecules induce additional mechanical strains which, in turn, lead to further crystal cracking, the formation of more reactive sites, and rapid acceleration of the decomposition reaction. This occurs until such time as the products of decomposition actually suppress the growth of reacting nuclei, causing the reaction to slow down abruptly, ultimately leading to an apparent unimolecular process [10-12,19]. Basic lead styphnate RD 1349 is highly crystalline; hence, it is not surprising that it decomposes under controlled conditions by such a mechanism.

Were the samples of basic lead styphnate in a less crystalline or amorphous form, it is quite possible that the kinetics of its thermal decomposition reaction could have followed a different rate law, as it is well known [3,10,11,21] that the physical order of the solid state does play a significant part in determining the pathway of many reactions. It has been observed, for instance, that the rate laws observed in the thermal decomposition reactions of mercuric fulminate [1,3] and of silver oxalate [3] depend on the condition and age of the materials - be they crystalline, crushed or very finely powdered - a greater number of lattice defects or discontinuities characterising the more amorphous powdered forms.

The implications of these observations to explosives science is obvious. Quite recently, it was shown [22-24] that many materials react to mechanical stimuli (impact, shock) producing a more-or-less localized distribution of "hot spots" and these hot spots are most likely associated with shear bands [25,26] and fracture sites (edges, discontinuities, glide planes, etc.) within the material [22,23].

Once these hot spots are created, the course of events depends on the nature and subsequent reactions of the substrate, the heat losses which may occur and the effects of adiabatic changes due to variations in pressure and volume within the crystal [27]. In short, traditional kinetic and thermochemical processes associated with controlled thermal decomposition reactions, such as described in this paper, come into play [23,28].

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Throughout this paper, basic lead styphnate (1) and normal lead styphnate (2) have been referred to by their commonly known names.

In Chemical Abstracts, (1) is now listed as [2,4,6-trinitro-1,3-benzene diolato (2)] di-lead hydroxide (Registry No. 12403-82-6); (2) is listed as lead (2+) [2,4,6-trinitro-1,3-benzene-diolate] monohydrate (Registry No. 66778-13-0).

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