Thermochimica Acta, 154 (1989) 247–253
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

REACTIVITY OF THE TERNARY FUSE HEAD SYSTEM LEAD 2,4-DINITROPHENOLATE–LEAD DIOXIDE–ALUMINIUM

SUDHIR ACHAR and SOMNATH GANGULY

IDL-Nitronobel Basic Research Institute, P.O. Box. 397, 18th. Cross, Malleswaram, Bangalore 560 003 (India)

(Received 16 March 1989)

ABSTRACT

The reactivity of the ternary system lead 2,4-dinitrophenolate–lead dioxide–aluminium has been studied in comparison with the binary system lead 2,4-dinitrophenolate–lead dioxide using differential scanning calorimetry. It was observed that the heat evolved per unit mass of LDNP increased with increasing lead dioxide content for both the binary and the ternary systems. Aluminium imparts an acceleratory effect on the reaction between lead 2,4-dinitrophenolate and lead dioxide without altering the decomposition pattern. Fourier transform IR spectra of undecomposed material were compared with those of the residue and the results were correlated with the thermal analysis data.

INTRODUCTION

Fuse head, electrical match head or squib is a flashing (igniting) element used in electric blasting caps and detonators. It is a combination of bridge wire, igniter composition (drop or cylindrical charge) and lead-in wires. Some squib compositions consist of lead 2,4-dinitrophenolate (hereafter denoted LDNP) and lead dioxide in admixture with zirconium where zirconium functions as a flame sensitizer. The major problems associated with the use of zirconium are its poor atmospheric stability and the hazards involved in its handling. The addition of aluminium to increase the performance of explosives was first proposed by Escales in Germany in 1899 and patented by Roth in 1900 [1]. The use of aluminium powder in some primary and ignition compositions was proposed in 1906 by Venier [2]. Other ingredients of such compositions were mercury fulminate, potassium chlorate, potassium picrate and silver acetylide. Sakamaki patented a composition for use in electric detonators [3]. The composition was lead dinitroresorcinate 55%, lead perchlorate 10%, sulphur 10%, aluminium 10% and binder 5%. The literature reports only the ignition temperature of LDNP and its preparation. Mass spectral and thermal studies on the explosion of LDNP were recently reported [4] where the deflagration of LDNP was

0040-6031/89/$03.50

contained to an extent such that DTA thermograms could be recorded. This was achieved by diluting LDNP with lead dioxide which also reacts with LDNP as a flash enhancing agent. This finds application in fuse heads where a sustained gaseous reaction accompanied by a flame is required to continue the explosive train. In our present work we have explored the possibility of using aluminium in place of zirconium. The acceleratory effect of aluminium on the reactivity of the binary system of LDNP and lead dioxide has been studied using differential scanning calorimetry and FTIR spectroscopy.

MATERIALS AND METHODS

LDNP was prepared by the addition of a solution of lead nitrate to sodium 2,4-dinitrophenolate in an alkaline medium at 80 °C. The fine precipitate was washed with water and stored in a methanol-wet condition. While it is possible to obtain continuously variable stoichiometries of the basic salt, the alkali content was adjusted so as to give the approximate composition $(C_6H_3N_2O_5)_2Pb \cdot 2PbO$.

AnalaR grade lead dioxide was used. Aluminium in the presence of water in a strongly oxidizing medium can make the explosive deteriorate and can also create danger through heating and gassing. To avoid this reaction, aluminium flakes coated with 0.5% stearic acid were used [5].

Because the mixtures are highly explosive, adequate safety precautions were taken during mixing, which was usually carried out by sieving the ingredients together in appropriate sieves behind safety screens.

Differential scanning calorimetry

Thermograms were recorded using a Perkin–Elmer model DSC-2C differential scanning calorimeter. Nitrogen was used as the purge gas. Samples were in aluminium pans and the lids were placed on without crimping. The heating rate used was 10 °C min^{-1} and the sensitivity was 20 mcal s^{-1}. The instrument was calibrated using samples of indium and tin which were supplied with the unit.

FTIR spectroscopy

FTIR spectra were recorded on a Bruker IFS-85 FTIR spectrophotometer coupled with an Aspect 2000 computer for data acquisition and analysis. One hundred scans were co-added to give a resolution of 2 cm^{-1}. Spectra were recorded with samples in the form of 0.5% KBr pellets.

RESULTS AND DISCUSSION

Binary systems

LDNP–lead dioxide system

LDNP and lead dioxide were dried in a vacuum oven at 80°C for 3 h. LDNP was mixed with different parts by weight of lead dioxide as shown in Table 1 and the mixtures were thoroughly homogenized. DSC thermograms were recorded for all the mixtures. The sample mass, peak temperatures and the measured heat evolved are tabulated in Table 1 and DSC curves for the mixtures are depicted in Fig. 1.

The DSC record of pure LDNP shows an exotherm commencing at 505 K leading to a peak at 556.7 K. The decomposition is complete at 570 K. For all the other mixtures, the exotherm begins around 506–508 K. The thermogram for sample 2 follows an exactly similar pattern with the peak shifted to 560 K. For sample 3 the main exotherm shows a shoulder in the lower temperature range at 550 K. The shoulder becomes more and more prominent as the lead dioxide content increases, which suggests the complexity of the decomposition pattern. It is interesting to observe that the decomposition range increases with increase in lead dioxide.

The actual quantity of LDNP for constant sample weight progressively decreases as the lead dioxide content increases. Hence, the heat evolved during decomposition should be calculated on the basis of unit mass of LDNP. It should be noted that the heat evolved per unit mass of LDNP increases progressively as the lead dioxide content increases (Table 1). However, the heat evolved per unit mass of the mixture decreases.

LDNP–aluminium system

LDNP was mixed with different parts by weight of aluminium. Thermograms of these samples were similar to that of pure LDNP except that the peak temperatures were shifted to 555, 554, 553, 553 and 552 K, and the

TABLE 1

DSC data for LDNP–PbO_2 mixtures

Sample number	Composition LDNP–PbO_2	Sample weight (mg)	Peak temp. (K)	Heat evolved per g of mixture (cal)	Heat evolved per g of LDNP (cal)
1	1:0	3.80	556.7	156.3	156.3
2	4:1	7.20	560.0	137.6	172.0
3	2:1	7.20	550.0, 564.0	120.0	179.5
4	1:1	7.13	547.0, 569.0	112.0	239.9
5	1:2	6.94	550.0, 575.0	103.0	309.1
6	1:4	7.10	533.0, 590.0	87.5	437.5

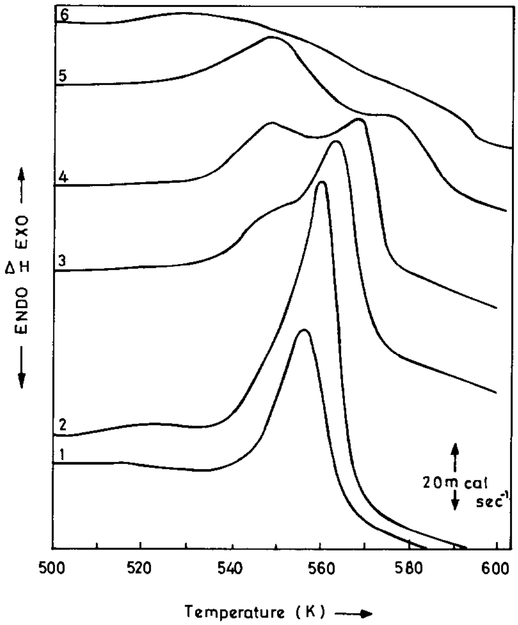

Fig. 1. DSC curves for binary mixtures of LDNP with lead dioxide. See Table 1 for compositions.

heat evolved per g of LDNP was 138, 128, 124, 118 and 101 calories for the LDNP–aluminium mixtures 4 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 4 respectively. The decrease in the heat evolved as the proportion of aluminium is increased may be due to a decrease in oxygen balance of the mixture. There is no significant interaction between the metal and LDNP.

Lead dioxide–aluminium system

Thermograms of mixtures of lead dioxide and aluminium did not exhibit any exotherm up to 600 K.

FTIR spectra

Figure 2 shows the FTIR spectrum of LDNP in the 2000–400 cm^{-1} region. Figure 2b is the spectrum of the compound after it was heated to 600 K on the DSC in nitrogen atmosphere (thermogram in Fig. 1). The spectrum shows a strong band at 1590 cm^{-1} due to the aromatic ring stretch and a band due to skeletal ring vibrations at 1400 cm^{-1}. The origin of the band at 547 cm^{-1} is not known. It is obvious from the spectrum that the decomposition of LDNP is incomplete when it is heated in nitrogen atmosphere at a rate of 10 °C min^{-1}. Figure 2c is the spectrum of a mixture of LDNP and lead dioxide (2 : 1) that was heated to 600 K under similar conditions. The spectrum shows only a strong band at 1400 cm^{-1} resulting from skeletal

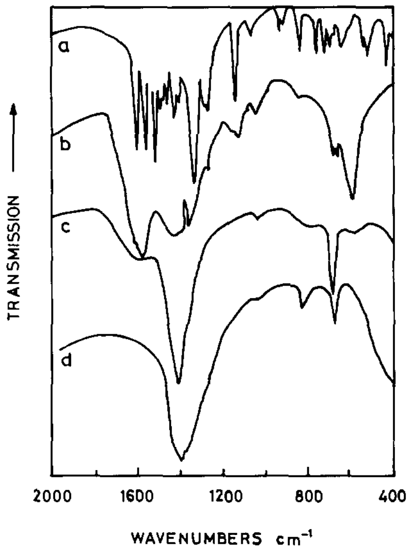

Fig. 2. FTIR spectra in the 2000–400 cm^{-1} region: a, pure LDNP; b, residue of LDNP; c, residue of (2 : 1) LDNP and lead dioxide; and d, residue of (1 : 2) LDNP and lead dioxide.

vibrations and a weak shoulder at 1600 cm^{-1} resulting from a small fraction of undecomposed ring material. A band is seen at 682 cm^{-1} resulting from CO_2 caused by decomposing ring material. When a mixture of LDNP and lead dioxide in the ratio (1 : 2) is heated to 600 K, the spectrum shows only a band due to skeletal ring vibrations at 1400 cm^{-1}. A band is also seen at 682 cm^{-1} due to CO_2 which derives from decomposing ring fragments (Fig. 2d). It is clear that heating LDNP with lead dioxide changes the decomposition pattern of LDNP and causes complete decomposition of undecomposed ring fragments. The decomposition of ring fragments in the presence of the oxide could probably have caused the appearance of the second exotherm in Fig. 1.

LDNP–lead dioxide–aluminium system

The binary mixtures corresponding to 2, 3, 4, 5 and 6 in Table 1 were mixed with 15 parts by weight of aluminium and the mixtures were homogenized. DSC thermograms for these were recorded (Fig 3). Table 2 lists the sample weight, peak temperatures and the heat evolved per unit mass of LDNP.

DSC curves of these samples show an exotherm commencing at around 495 K. The traces follow a similar pattern as those for the LDNP–lead dioxide system except that the inception and peak temperatures are shifted to lower temperatures for the ternary system indicating the accelerating effect of aluminium. It can be seen that the heat liberated is more for aluminized compositions and it increases with increasing lead dioxide (Table 2).

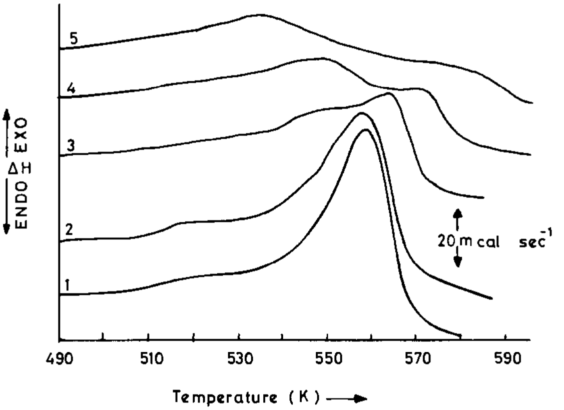

Fig. 3. DSC curves for ternary mixtures of LDNP with lead dioxide and aluminium. 15 parts by weight of aluminium were added to the binary mixtures 2 (curve 1), 3 (curve 2), 4 (curve 3), 5 (curve 4) and 6 (curve 5) given in Table 1.

DSC thermograms were also recorded as a function of aluminium content in the basic composition 1 : 1 LDNP and lead dioxide (Fig. 4). Curves a, b, c and d correspond to the mixture of 6 mg of 1 : 1 LDNP and lead dioxide with 1.5, 3.0, 6.0 and 9.0 mg aluminium respectively. For the sample with the lowest aluminium content, the main reaction exotherm shows a well-defined shoulder at 545 K followed by a peak at 563.5 K. The intensity of the former decreases as the proportion of aluminium increases. The peak temperature shifts to 562, 560 and 555 K for curves b, c and d respectively with increasing aluminium content.

From the inception and peak temperatures, it is obvious that aluminium accelerates the reaction between LDNP and lead dioxide without altering the decomposition pattern. The complete characterization of the reaction is in progress.

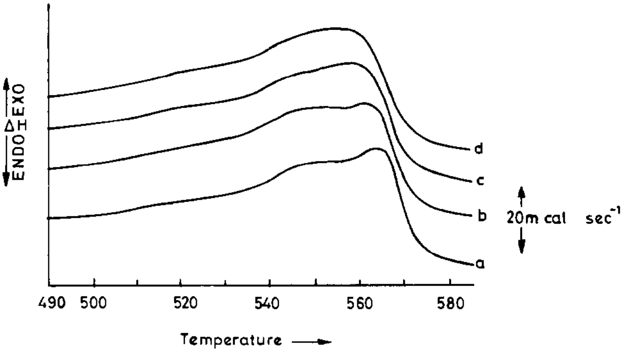

Fig. 4. DSC curves for mixtures having different aluminium contents in the basic composition of 1 : 1 LDNP : lead dioxide. Aluminium contents in 6 mg of 1 : 1 LDNP: Lead dioxide: a, 1.5 mg; b, 3.0 mg; c, 6.0 mg; d, 9.0 mg.

TABLE 2

DSC data for LDNP–PbO_2–aluminium mixtures

Curve no.	Sample weight (mg)	Peak temperature (K)	Heat evolved per g of mixture (cal)	Heat evolved per unit mass of LDNP (cal)
1	6.46	557	176.0	220.0
2	6.97	557	157.3	236.9
3	6.00	544, 563	133.3	266.7
4	6.50	545, 569	117.5	352.4
5	7.20	533, 580	112.2	561.7

CONCLUSIONS

DSC studies on the binary system LDNP–lead dioxide show an increase in the heat evolved per unit mass of LDNP and a shift to lower temperatures of the decomposition peak. Studies on the binary systems aluminium–LDNP and aluminium–lead dioxide do not indicate any significant interaction between the metal and LDNP or the oxide. The results of the studies on the ternary system aluminium–lead dioxide–LDNP clearly show an acceleratory effect of the metal on the lead dioxide–LDNP reactivity. The heat evolved per unit mass of LDNP is higher for this system and the initiation temperatures are lower when compared to the LDNP–lead dioxide system. The ternary system is promising and can be used as a fuse head composition in electric detonators.

ACKNOWLEDGEMENTS

The authors wish to thank IDL Chemicals for allowing publication of this work, Mr. R. Vedam, General Manager, INBRI for encouragement and the late Dr. S.R. Yoganarasimhan, Dr. V. Krishna Mohan, Dr. P.L. Hariharan for useful discussions.

REFERENCES

1 G. Roth, Ger. Patent 172,327 (1900).
2 W. Venier, Brit. Patent 6,705 (1906) and Chem. Abstr., 1 (1907) 929–30
3 T. Sakamaki, Jpn. Patent 147 (51) and Chem. Abstr., 46 (1952) 11690.
4 S.R. Yoganarsimhan, G.O. Reddy and S. Achar, J. Energ. Mater., in press.
5 T. Urbanski, Chemistry and Technology of Explosives, vol. 4, Pergamon, Oxford, 1984, p. 518.