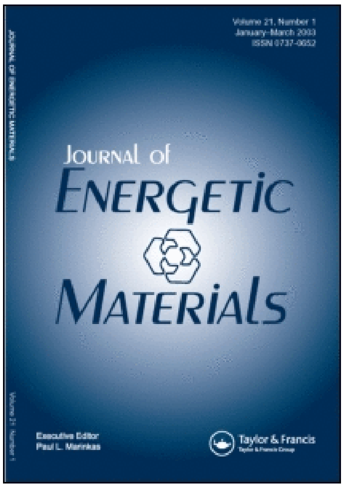

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Mass spectral and thermal studies on explosion of lead salts of picramic acid and 2,4-dinitro phenol

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MASS SPECTRAL AND THERMAL STUDIES ON EXPLOSION OF LEAD SALTS OF PICRAMIC ACID AND 2,4-DINITRO PHENOL.

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ABSTRACT

The mass spectral studies on the slow decomposition and explosion of lead salts of 2,4 -dinitrophenol and 2-amino-4, 6-dinitrophenol show distinct differences in the reaction pathways of the two salts. The low temperature decomposition occurs in two stages of an explosion following a slow decomposition, where as both salts explode in an overlapping complex pattern at high temperatures. The decomposition pathways are predicted by analysing the fragmentation patterns. The results are suggestive of first step of the reaction to be a rupture of the Pb-O linkage. Thermal studies supplementing the mass spectral data show that lead picramate is more brisant than lead salt of 2,4 dinitrophenol. This is attributed to a higher degree of covalency of the Pb-O bond in picramate relative to dinitro phenolate.

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INTRODUCTION

A knowledge of explosive decomposition of lead salts of nitrophenols is important from the point of view of their application in explosive devices. 2,4,6 - trinitro-1, 3-benzene-diol lead salt (commonly called lead styphnate, LS) has been studied in some detail and 2,4 - dinitro-1, 3-benzene-diol lead salt (Lead dinitro resorcinate, LDNR) has been only recently studied even though the compound is being used in ignition compositions for about 50 years. Time resolved mass spectroscopy by electron impact has been effectively used to predict the reaction pathways of LS[1] and LDNR[2]. The concept of similarity in reaction pathways of explosive decompositions and those under electron impact conditions originally emanated from Torsell and Ryhage[3] who predicted the likely reaction paths during the pyrolysis of aliphatic nitro compounds. Meyerson et.al[4] were of the view that the primary loss of NO_2 group was rate controlling during the decomposition of unsubstituted 1,3,5 - trinitrobenzene. Further substitution on the benzene ring, however leads to different reaction pathways including a loss of OH through a cyclic intermediate.[5] Such mechanisms impart enhanced reactivity particularly during the initial stages of explosive reactions of metal salts of nitrophenols when subjected to low magnitude of external stimuli.

In this context, more detailed studies of lead nitrophenolates are warranted to understand the reaction pathways and initial products of decomposition under such conditions as close to explosive reaction as possible. We have chosen 2,4 - dinitro benzene -1-ol lead salt (LDNP) and 2-amino -4,6-dinitro, benzene-1-ol lead salt (Lead picramate, LPa) for our study because both these compounds are used in fuse head compositions in electric detonators. Only ignition temperatures of both and preparation and characterization of the latter[6] are available in the published literature. There is an additional complexity in LDNP because it gets precipitated invariably as a basic salt of variable stoichiometry. Therefore data on characteristics of LDNP of undefined stoichemetry needs a thorough scrutiny. The addition of an electron donating group in ortho position with respect to hydroxyl group is expected to significantly alter the reaction because of its proximity to the primary reaction centre. The present work concerns with mass spectrometric studies of explosive decomposition of LDNP and LPa using double focusing magnetic sector high resolution instrument which enables detection of all the mass numbers within a duration of 1 sec at any given stage of decomposition as determined by a preset scan in the total ion current chromatogram. The earlier mass spectral studies[1,2] were confined to low mass numbers. But one should expect higher mass numbers also in the fragmentation arising from explosion. We have extended the mass region to beyond the mass number of lead. Tang[2] could not observe any peaks above m/z of 75 and concluded that Pb^+ or Pb^{++} are not formed which is taken as a proof of pure solid state reaction without evaporation in the case of LDNR. We have on the contrary recorded mass numbers equal to lead and also those of adduct products of lead with other fragmentation species.

A second objective of these studies is to smoothen the deflagration of the LDNP and LPa to an extent possible in order to record the thermograms. This is achieved by diluting the compounds with PbO_2 which also reacts with them as a flash enhancing agent. This finds application in fuse heads where a sustained gassy reaction accompanied by a flame is required to continue the explosive train. DTA of the two compounds in the presence of PbO_2 has helped in demonstrating the effect of the o-amino group on the reactivities of the lead salts.

MATERIALS AND METHODS

LDNP was prepared by the addition of a solution of lead nitrate to sodium 2,4-dinitrophenolate in alkaline medium at 80° C. The fine precipitate was washed with water and preserved in methanol wet condition. While it is possible to obtain continuously variable stoichiometries of the basic salt, the alkali content was so adjusted as to give an approximate composition $(C_6H_3N_2O_5)_2$ Pb.2PbO.

LPa was also prepared by a similar method using lead nitrate and sodium picramate. Analysis of the nitrogroups by $TiCl_3$ titration method showed that the salt was more than 98% pure.

Mass Spectrometry

Mass spectra were recorded on a JEOL - DX 300 double focussing magnetic sector high resolution mass spectrometer coupled to SN-23 computer for data aquisition and analysis. The sample was introduced into the direct insertion (DI) probe with heating facility. Sample temperature could be fixed at any value between ambient and 350° C. Ionization current was scanned every second between mass range of 50 and 500 a.m.u. The instrument was calibrated with perflurokerosene prior to the sample analysis. A few micrograms of the sample were taken in a capillary tube, inserted into the DI probe and heated at a predetermined rate to a final temperature of 250° C or 350° C.

Thermal Analysis

Thermograms were recorded in nitrogen atmosphere using Perkin Elmer DSC-2C. DTA thermograms were recorded in air using a DTA unit with a Stanton Redcroft linear temperature programmer, a home made sample holder of platinum cups fused to Pt/Pt-13% Rh thermocouple and a two channel strip chart recorder. Heating rate was 10°/min.

RESULTS AND DISCUSSION

I. Mass Spectral Studies

Mass spectra of the parent compounds 2,4-dinitrophenol (DNP) and 2-amino- 4,6-dinitrophenol (picramic acid) were recorded to obtain a clue to the likely fragmentation pattern of their lead salts. DNP is known to sublime slowly above 70° C, melt at 113-114° C and evaporates thereafter. A rapid rate of heating was therefore employed. Picramic acid melts at 169-70° C.

A. Decomposition Pathways of the Parent Compounds

The mass spectra of DNP (a) and picramic acid (b) recorded under identical conditions of operation are shown in Fig.1. The mass numbers and their relative intensities are listed in Table 1. Variations in probe temperature, heating rate and chamber temperature did not alter the pattern of fragmentation. The parent ion $(M)^{+}$ of DNP, which is also the base peak seems to be more stable than the parent ion (M^{+}) of picramic acid which gives the base peak at a mass number of 78. The suggestive fragmentation pathways in the two cases are given in Scheme 1. The likely assignments for lower mass numbers which manifest as fine structure have not been made as there could be a number of possibilities. The observed m/z = 62 in both cases could be probably assigned to nitrate groups. Some important discernible differences between the fragmentation pathways are the following.

1. The loss of NO_2 group from DNP seems to take place in two distinct steps of losses of O and NO. The existence of relatively strong 154 and an extremely weak 138 is suggestive of the two step process. On the contrary a single step loss of NO_2 yields a relatively intense m/z = 153 in the case of picramic acid.

TABLE 1

Species Evolved From Fragmentation Of DNP And Picramic Acid

DNP		Picramic acid	
m/z	Abundance	m/z	Abundance
184	100	199	83
168	5	182	6
154	35	153	20
138	<5	122	23
107	30	106	68
91	35	94	43
79	25	78	100
62	50	62	25

2. The existence of a species corresponding to m/z value of 182 during fragmentation of picramic acid suggests a loss of OH radical. Such a possibility could be anticipated in the light of the fragmentation pattern of 2,4 - dinitroanilino acetic acid reported by Rao and Yoganarasimhan.[5]

3. Interestingly, the base peak in mass spectrum of picramic acid coresponds to an ion of m/z = 78. This suggests that the parent M^{+} undergoes fast fragmentation yielding finally the base peak. By contrast DNP seems to give a parent ion as base peak.

4. DNP probably decomposes by a series of relatively slow multistep processes as against the likelihood of single step primary process in picramic acid. This conclusion is reached by the comparison of the total ion current (TIC) chromatograms (Fig.2). DNP is thus believed to be more stable than picramic acid

under electron impact conditions. Thermal analysis also indicated similar trend. Picramic acid shows an exotherm around 230° C while DNP gives an exotherm at 360° C only when the DTA of DNP/Al_2O_3 = 1/3 is recorded. In the absence of alumina DNP completely evaporates before attaining the decomposition temperature.

B. Decomposition Pathways for the Lead Salts

(i) LPa

The TIC chromatograms obtained at low temperature (250° C) and high temperature (350° C) during the decomposition of LPa are shown in Fig 3. The low temperature TIC is characterised by a broad peak representing slow decomposition followed by a sharp peak representing a fast explosive decomposition. The high temperature TIC shows a single sharp peak corresponding to the explosive decomposition. The mass spectrum recorded at Scan No 149 during the slow decomposition shown in Fig.4a is similar to that of Picramic acid as in Fig.1b. The main difference is that the base peak has an m/z value of 199 $(M-Pb+H)^+$. Though the mass spectrum of explosive decomposition at 350° C (Fig.4c) has some important characteristics in common with the mass spectrum recorded at Scan no 149 during slow decomposition at 250° C as shown in Fig.4a, it has many features in common with the mass spectrum at Scan no 223 during fast decomposition at 250° C (Fig.4b). Several mass numbers beyond 199 can be seen in them. These spectra clearly suggest that lead picramate decomposes by at least two steps at low temperatures and by overlapping fast processes during an explosion at high temperatures when extreme fragmentation of the molecule takes place. It is possible to obtain mass numbers corresponding to Pb^+ and several adduct species of Pb with other fragmentation products. The base peak (m/z 55) on explosion probably arising from excessive fragmentation corresponds to C_2HNO unlike in the explosion of lead styphnate.[1] The adduct of Pb(208) and a.m.u 52 (C_2N_2) in the transient phase can give m/z of 260 which is observed in Fig 4c. A.m.u of 52 was also observed during the explosive fragmentation of the related compound LS in time resolved mass spectroscopy.[1] When an explosion occurs following a slow decomposition as in Fig.4b, the stability of peak at a.m.u 199 decreases. One significant feature during the explosive decomposition of LPa is that the picramic acid portion gets detached from the lead and it is suggestive of the first rupture occuring at the Pb-O bond which is supposed to be partly ionic. The suggested explosive decomposition parthways are shown in Scheme 2.

(ii) LDNP

Just as in the case of LPa, TIC at low temperatures showed a broad peak followed by a sharp explosive decomposition peak. A single sharp peak dominated the TIC at 350°C. The mass spectrum of the broad peak which is not shown, was similar to that of pure DNP (Fig 1a). The mass spectra of the species produced by fast decomposition at both temperatures shown in Fig.5 have mass numbers higher than M^+ of DNP and are therefore expected to be transient adducts of lead with the fragmentation products. The intensity at 184 $(M - Pb + H)^+$ is extremely low in both cases. So is the intensity of this mass number during the slow decomposition. This is suggestive of an almost concurrent cleavage of Pb-O linkage and the loss of O and NO groups. The base peak in all the cases is at m/z of 62 which could be C_4N or NO_3. It has not been possible to identify which one it is. The reaction pathway for the decomposition of LDNP is similar to that of DNP with the possible Pb-O cleavage taking place concurrently.

II Thermal Studies

The objective of the thermal studies is to study the relative powers of the two lead salts in the formulations which are used in squibs without any other additional metallic fuel. Though DSC of the pure compound could be easily recorded for e.g LPa in Fig 6, the value of this in a heretogeneous reaction is rather limited because of sample size effects. Larger quantities shatter the instrument. Therefore the reactivity of LPa and LDNP with PbO_2 which is a common squib component, is taken as the criterion. The deductions are purely qualitative but still valuable in providing the guidelines to an explosives development scientist.

DTA of pure LPa and LDNP could not be recorded above a sample size of 2-3 mg because the material exploded in the sample cup. The instrument was insensitive to record the small heat changes below a sample mass of 1 mg. The DTA of mixtures with Al_2O_3 were not truly reproducible due to thermal conductivity problems. The DTA of mixtures with PbO_2 are shown in Fig.7. LDNP and PbO_2 reacted smoothly at a mass ratio of 1 : 10 and 1 : 15 giving well defined broad exotherms around 265° - 270° C, LPa gave sharp exotherms around 265° - 280° C accompanied by flash and sound even at lower sample mass. This definitely suggests that LPa is more brisant than LDNP.

The effect of Amino Group

The foregoing results show that LPa which has an amino group ortho to the phenolic group is thermally less stable than LDNP and undergoes a higher degree of fragmentation during explosion. It would be interesting to contrast this behaviour with those of amino nitro benzenes. Mass spectral observations of sym-trinitrobenzene by Meyerson[4] showed that the first step of fragmentation is the elimination of NO_2 group. The compound has much lower thermal stability and low initiation threshold to shock relative to TATB (1,3,5 - triamino -2,4,6-trinitrobenzene) which has a very high threshold to shock besides being a high temperature explosive. Addition of the amino group to nitrobenzenes will have a bond strengthening effect on the ring C - C bonds by donation of electrons, thus compensating for the nitrogroup electron withdrawal.[7] However, in the case of nitrophenols, the addition of aminogroup has the opposite effect. Though mass spectral studies suggest a primary step involving cleavage of Pb-O linkage in both cases, the influence of the steric factor of o-amino group on the relative stability of Pb-O linkage should be considered. C^{13} chemical shifts for o-, m- and p-amino groups relative to 1 positioon proton are -13.8 δ, +0.9 δ and -9.8 δ respectively.[8] The inductive effects are thus negligible. Assuming the resonance contributions from o and p are -9.8 δ, a difference of -4.0 δ which is nearly 40% of resonance contributions, could be attributed to steric factors. The effect of o-amino group on a phenolic group is expected to be higher still. The observable effect of such factors would be a weakening of the Pb-O bond in lead picramate resulting in higher thermal sensitivity of the compound. Sensitization of the azides by an increase of the covalent character of the metal-azide bond is a well known fact. Sensitization observed in lead picramate probably arises from a combination of increased covalency and steric factors.

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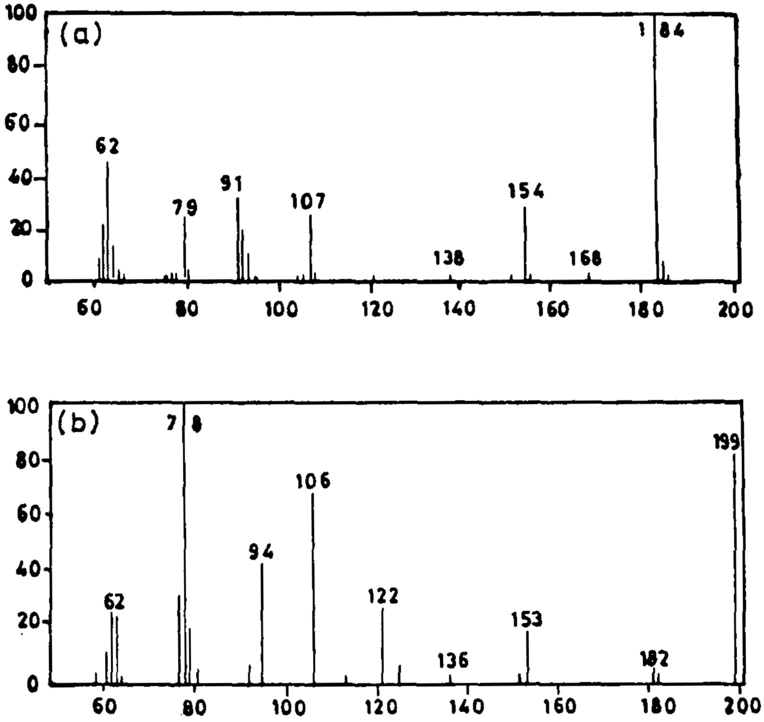


FIGURE - 1

Mass spectra of (a) 2,4-dinitrophenol and (b) picramic acid.

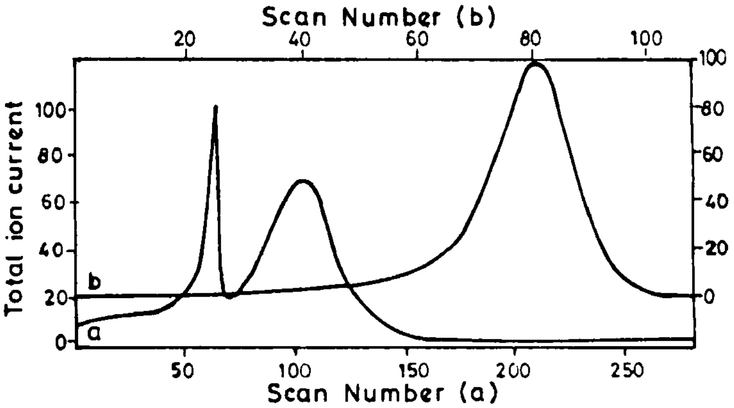


FIGURE - 2

Total ion current chromatogram of (a) 2,4- dinitro phenol and (b) picramic acid.

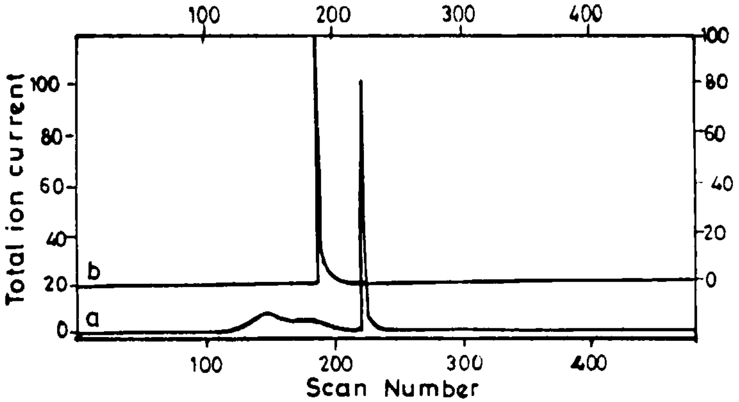


FIGURE - 3

Total ion current chromatogram during fragmentation of lead picramate at (a) 250 °C and (b) 350 °C.

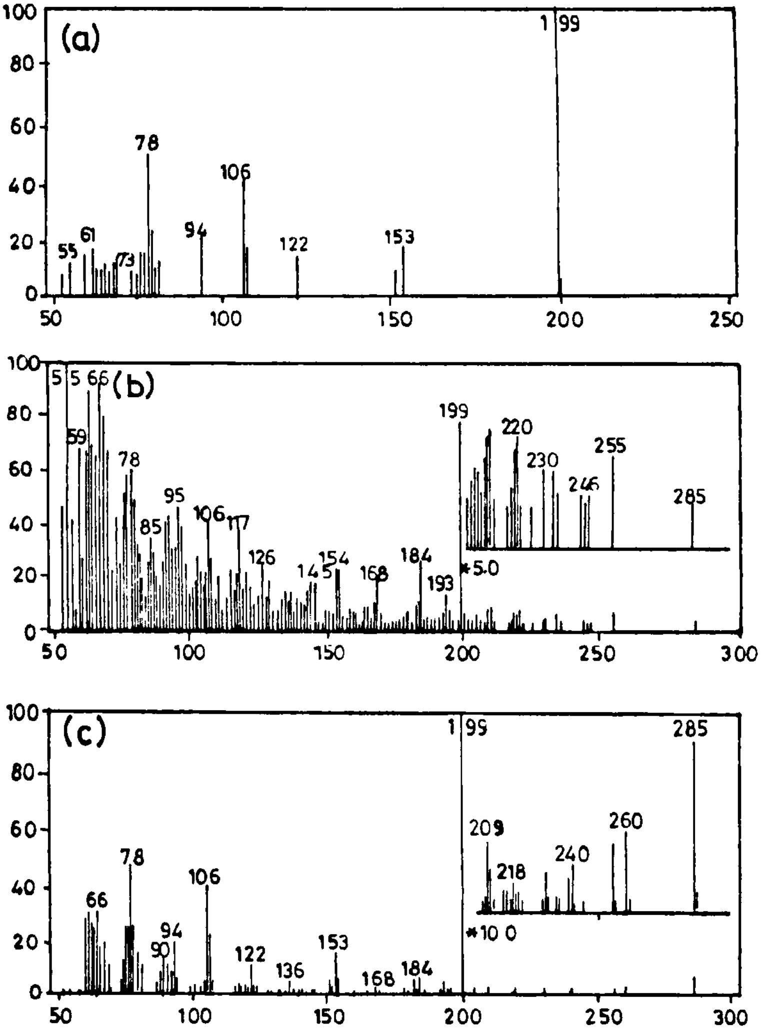


FIGURE - 4

Mass spectra of lead picramate (a) 250° during slow decomposition (scan no 149), (b) fast decomposition (scan no. 223), (c) explosion at 350° C.

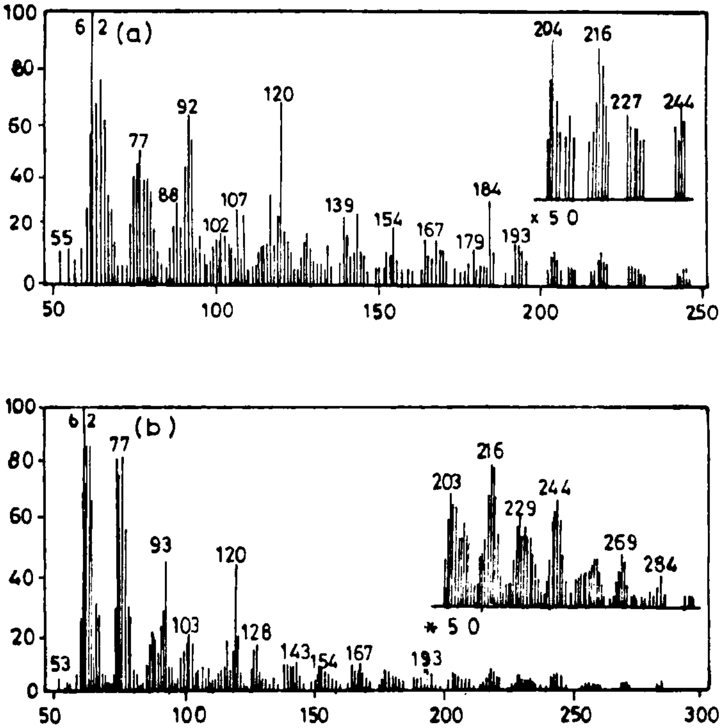


FIGURE - 5

Mass spectra of lead 2,4-dinitrophenolate during explosion at (a) 250° C and (b) 350° C.

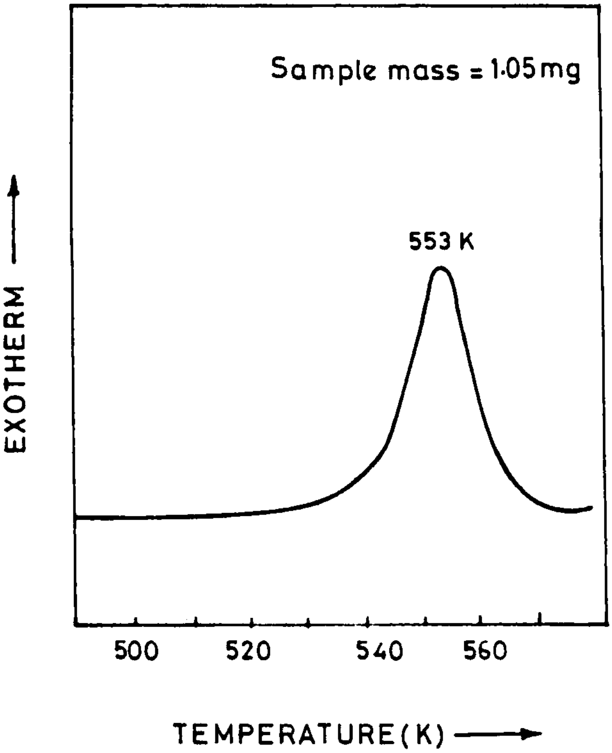


FIGURE - 6

DSC of lead picramate.

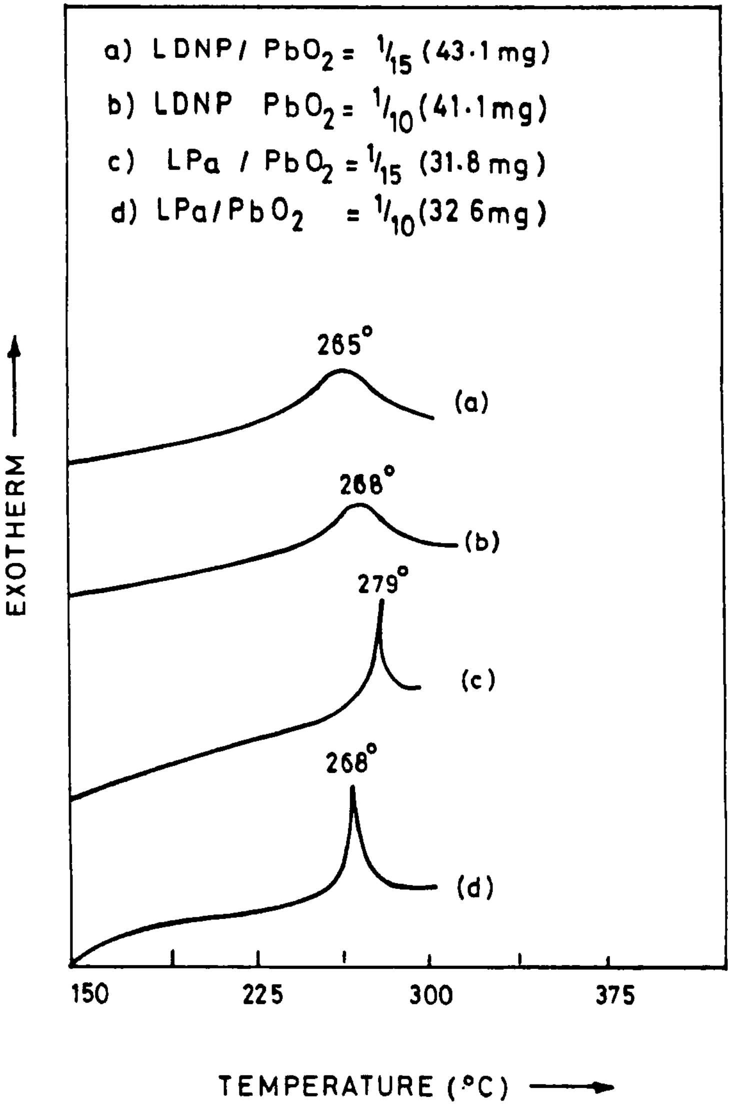
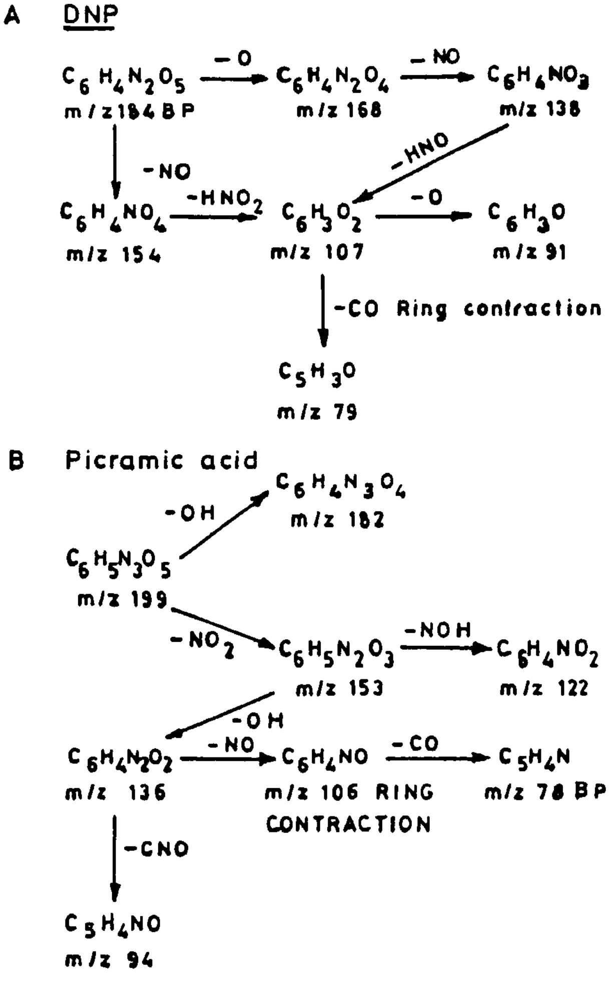


FIGURE - 7

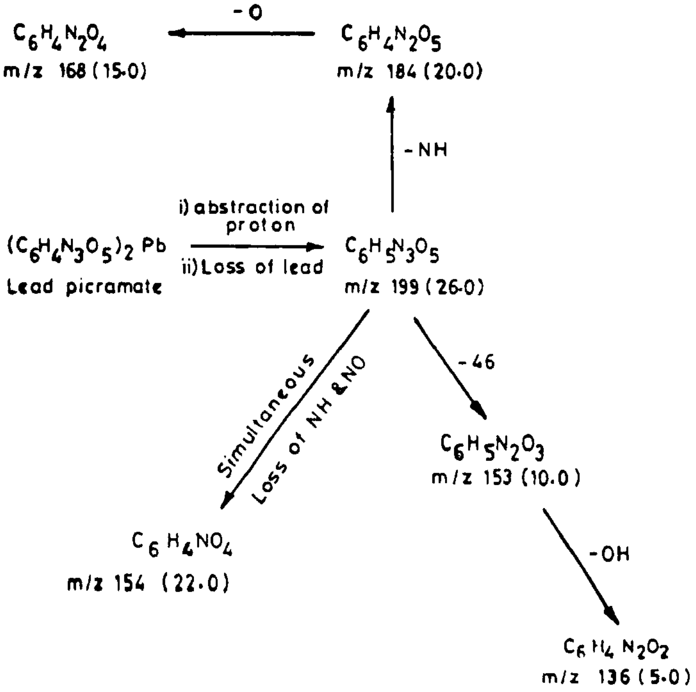
DTA

DTA of mixtures of lead 2,4 -dinitrophenolate and lead picramate with PbO_2.

Scheme 1


A
DNP
$C_6H_4N_2O_5$
m/z 184 BP
−O
$C_6H_4N_2O_4$
m/z 168
−NO
$C_6H_4NO_3$
m/z 138
−NO
−HNO
$C_6H_4NO_4$
m/z 154
−HNO$_2$
$C_6H_3O_2$
m/z 107
−O
C_6H_3O
m/z 91
−CO Ring contraction
C_5H_3O
m/z 79
B
Picramic acid
−OH
$C_6H_4N_3O_4$
m/z 182
$C_6H_5N_3O_5$
m/z 199
−NO$_2$
$C_6H_5N_2O_3$
m/z 153
−NOH
$C_6H_4NO_2$
m/z 122
−OH
$C_6H_4N_2O_2$
m/z 136
−NO
C_6H_4NO
m/z 106 RING CONTRACTION
−CO
C_5H_4N
m/z 78 BP
−CNO
C_5H_4NO
m/z 94

Scheme-2


$C_6H_4N_2O_4$
m/z 168 (15.0)
-O
$C_6H_4N_2O_5$
m/z 184 (20.0)
-NH
$(C_6H_4N_3O_5)_2$ Pb
Lead picramate
i) abstraction of proton
ii) Loss of lead
$C_6H_5N_3O_5$
m/z 199 (26.0)
Simultaneous Loss of NH & NO
-46
$C_6H_5N_2O_3$
m/z 153 (10.0)
$C_6H_4NO_4$
m/z 154 (22.0)
-OH
$C_6H_4N_2O_2$
m/z 136 (5.0)

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