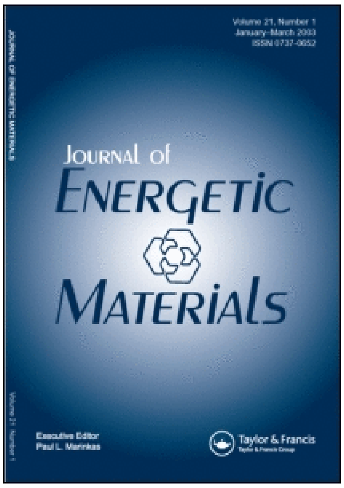

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Thermal characteristics of alkali metal dinitramide salts

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THERMAL CHARACTERISTICS OF ALKALI METAL DINITRAMIDE SALTS

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ABSTRACT

A thermal study of the dinitramide salts of lithium, sodium, potassium, rubidium and cesium is presented. The series displayed a complex set of DSC exothermic decays with the exception of the lithium salt which showed two simple exothermic decomposition reactions. All five salts thermally decomposed to the equivalent nitrate salt as evidenced by DSC melting endotherms and TGA stoichiometric mass losses. Physical changes due to thermal heating were

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able to be followed by hot stage microscopy. Thermal decay was accompanied by gas evolution.

INTRODUCTION

Investigations into the energetic oxidant ammonium dinitramide (ADN) (Figure 1) have been intensively carried out over the past decade and have been the subject of a number of patents[1] and scientific papers[2]. A chlorine-free high energy material, ADN is a potential replacement for ammonium perchlorate in rocket motors, leading to a reduced plume signature and chlorine-induced atmospheric ozone destruction. It also has the potential to replace ammonium nitrate, which possesses a lower energy content[3] as well as a low surface temperature and burn rate in rocket propellants[4]. ADN, however, is a reasonably hygroscopic material which can create handling difficulties and necessitate the use of coating agents. Additionally, the thermal stability of ADN is still questionable and may require the addition of various thermal stabilisers[5].

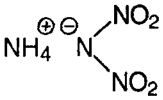

FIGURE 1. Structure of ADN.

As part of ongoing research into ADN, a series of alkali metal dinitramide derivatives were synthesised for trial in pyrotechnic flare compositions. Metal dinitramide salts not only provide an energetic oxidant for the composition, but also enable metal salts to be incorporated at a molecular level to provide pyrotechnic effects and increase the density of the final flare formulation. A large volume of Russian literature has appeared recently describing the synthesis of various metal dinitramide salts[6], however, very little has appeared describing the thermal characteristics of these compounds. In this investigation the thermal behaviour of lithium, sodium, potassium, rubidium and cesium dinitramide was examined by differential scanning calorimetry (DSC), thermal gravimetric (TG) and differential thermal (DT) analysis, with likely products of thermal decomposition identified.

EXPERIMENTAL

ADN was purchased from Thiokol and used as received. All samples were kept in a desiccator prior to use. All five salts were synthesised by reaction of ADN with the appropriate metal hydroxide[6]. Identification and purity of each salt was confirmed by melting point, mass spectrometry and microanalysis after recrystallisation. DSC experiments were performed on a Perkin Elmer DSC-7 instrument using uncrimped aluminium pans under an argon atmosphere at a ramp rate of 5°C/min. TG and DT analysis was performed on a Stanton Redcroft STA-1500 using open aluminium pans under an argon atmosphere at a ramp rate of 5°C/min. Powdered alumina was used as the TGA reference. Hot stage microscopy was performed on a Mettler FP21 Hot Stage at a ramp rate of 2°C/min with a 35x magnification.

RESULTS AND DISCUSSION

Lithium Dinitramide (LiDN)

The DSC trace of LiDN displayed two exotherms at 125°C (-298 J/g) and 182°C (-101 J/g) (Figure 2). The melting endotherm occurred between the two exotherms at 157°C (+83 J/g) and corresponds to melting of an initial decomposition product rather than LiDN itself. This was confirmed by hot stage microscopy where the salt was seen to first darken and then evolve gas before melting. LiDN is extremely hygroscopic and becomes hydrated within a short period upon exposure to the atmosphere. The DSC trace of a LiDN sample exposed to the atmosphere displayed an endotherm at 63°C (+52 J/g) corresponding to the loss at H_2O from LiDN.H_2O (LiDN.H_2O lit.[6c] mp 68-73°C) (Figure 3). TGA of this sample showed a three stage decomposition with mass losses corresponding to both exotherms plus the melting endotherm at 157°C (Figure 4). A total mass loss of 40.2% was observed corresponding to the formation of $LiNO_3$ from the dinitramide, with a stoichiometric loss of N_2O. Despite the suspected formation of $LiNO_3$, the corresponding nitrate melting point (264°C[7]) was not observed in either the DSC or DTA.

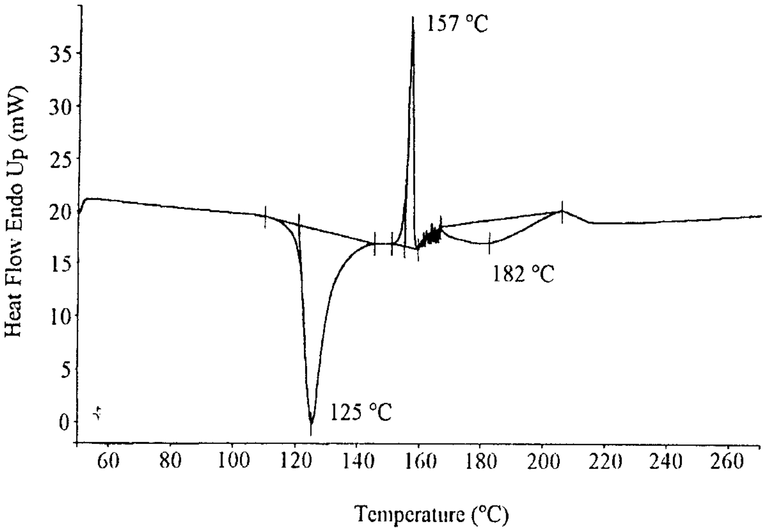

FIGURE 2. DSC Trace of LiDN.

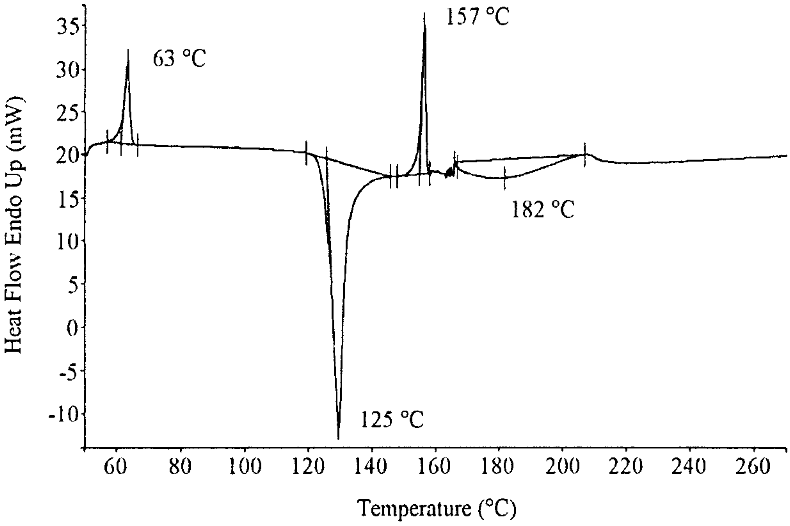

FIGURE 3. DSC Trace of LiDN.H_2O.

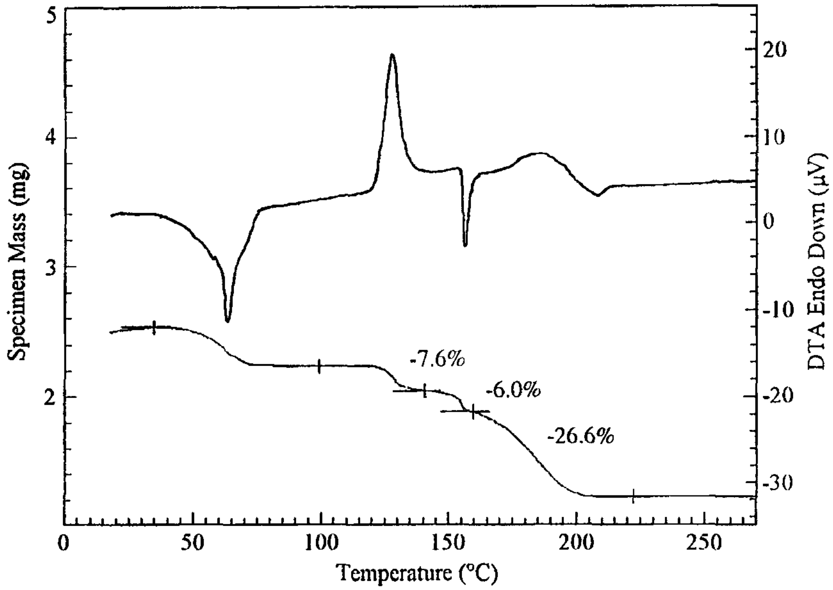

FIGURE 4. TGA Trace of LiDN. Mass losses calculated after initial water loss.

Sodium Dinitramide (NaDN)

The NaDN salt gave a DSC melting endotherm at 97°C (+54 J/g) followed by major and minor exotherms at 156°C (-946 J/g) and 210°C (-105 J/g) respectively (Figure 5). The minor exotherm at 210°C appeared just below the baseline and was confirmed by a corresponding TG mass loss. A third minor exotherm was observed in the DTA (Figure 6) just prior to melting (91°C) but was not evident in the DSC. TG analysis showed mass losses of 6.0, 25.7 and 6.4% for the three DSC/DTA exotherms and matched the stoichiometric formation of $NaNO_3$. Additional evidence for nitrate formation was observed in both the DSC and DTA traces as endotherms at 291°C (+61.1 J/g) for the melting of $NaNO_3$ ($NaNO_3$ lit.[7]

mp 307°C). The nitrate melting endotherm observed at 291°C was lower than the corresponding literature value, however, a significant depression in melting points for ADN and dinitramide salts is observed by the inclusion of small quantities of impurities[8], a situation which would be expected for the formation of nitrate salts *via* thermal decomposition. The exotherms at 156°C and 210°C correspond to those reported elsewhere[9].

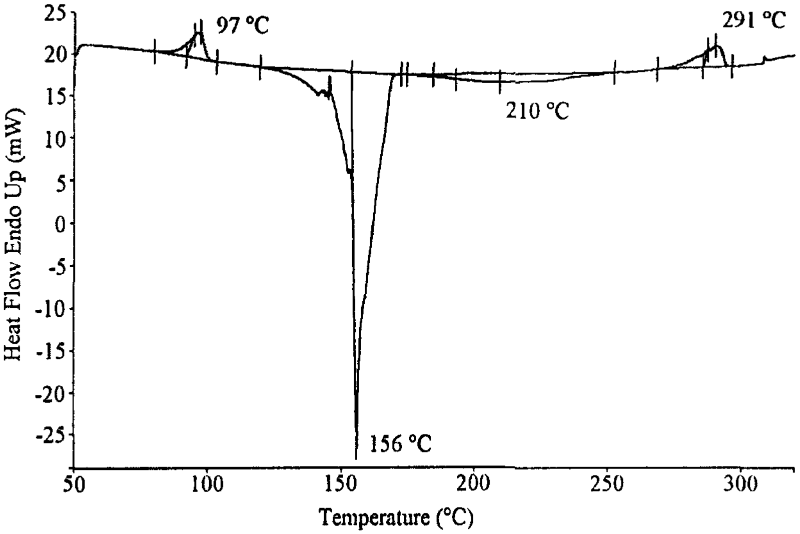

FIGURE 5. DSC Trace of NaDN.

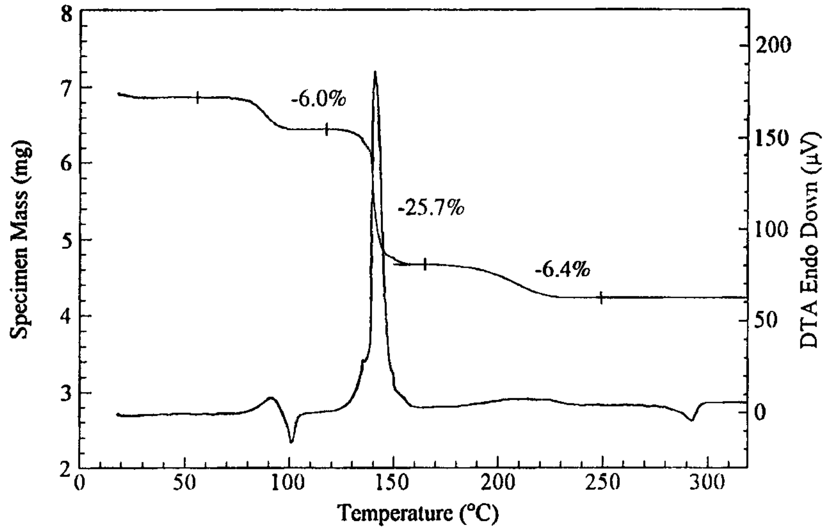

FIGURE 6. TGA Trace of NaDN.

Potassium Dinitramide (KDN)

The DSC trace recorded for KDN (Figure 7) was markedly different to that previously reported[9]. A large endotherm was observed at 128°C (+96 J/g) corresponding to melting of KDN[6c], however, it was preceded by a smaller exotherm (105°C, -10.5 J/g) and endotherm (108°C, +5.3 J/g). Hot stage microscopy showed the exothermic process from 92-108°C to be a breakdown of the crystal structure. The solid was then seen to partially melt from 109-115°C, after which no further decomposition or melting was observed until the onset of the KDN melt at 119°C. Thermal decay of the potassium salt is reported to commence prior to the solid melting (lit.[6c] mp 127-131°C) and continue to 115°C, as was observed here, at which stage reaction sites melt and the decay terminates[10,11]. The observed endotherm at 108°C corresponds to the melting point of the KDN/KNO_3 eutectic[10]. Two major exotherms were observed in the DSC, with the first displaying at least two overlapping maxima (range 140-182°C, -605 J/g).[11] The second exotherm occurred at 227°C (-101 J/g) and was consistent with that previously reported[8]. DSC thermograms reported by Oxley *et al* for KDN showed a single exotherm at 239°C with three overlapping peaks[8], however, lower scan rates revealed a more complex set of exothermic decay reactions. A final endotherm occurred at 319°C (+51.5 J/g) corresponding to melting of KNO_3, the final decay product (KNO_3 lit.[7] mp 334°C). TGA mass losses of 4.4, 15.3 and 10.5% were observed for the three exothermic decay reactions respectively (Figure 8). The total mass loss of 30.2% corresponded to the formation of KNO_3.

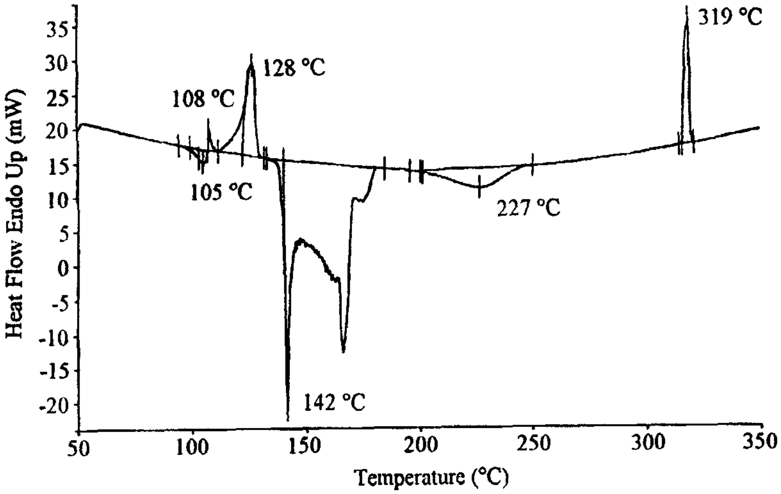

FIGURE 7. DSC Trace of KDN.

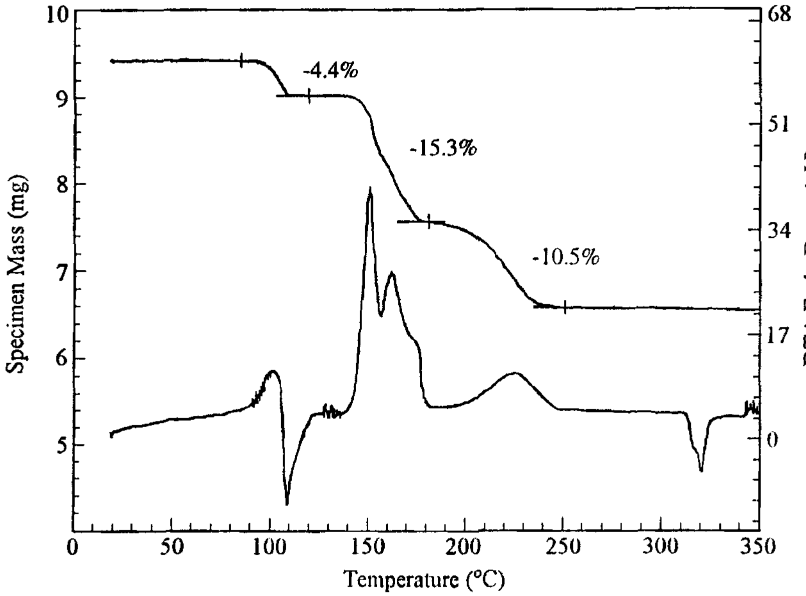

FIGURE 8. TGA Trace of KDN.

Rubidium Dinitramide (RbDN)

DSC analysis of RbDN gave a similar trace to both the sodium and potassium analogues (Figure 9). Two complex exotherms were observed at 141°C (-298 J/g) and 230°C (-60 J/g). The major endotherm observed at 104°C (+78 J/g) corresponds to melting of the dinitramide salt[6c]. A smaller endotherm was also observed at 85°C (+4.2 J/g). The TGA trace (Figure 10) showed no mass loss at this point, with the exotherm possibly due to a crystal phase change. Hot stage microscopy clearly showed internal rearrangement and fracturing of the crystal structure from 86.0°C until onset of melting at 100.3°C. Two thermal decays with mass losses of 10.8 and 17.5% respectively were observed in the TGA and correspond to the stoichiometric formation of the nitrate. Additionally, a melting endotherm was observed at 330°C (+295 J/g, $RbNO_3$ lit.[7] mp 310°C).

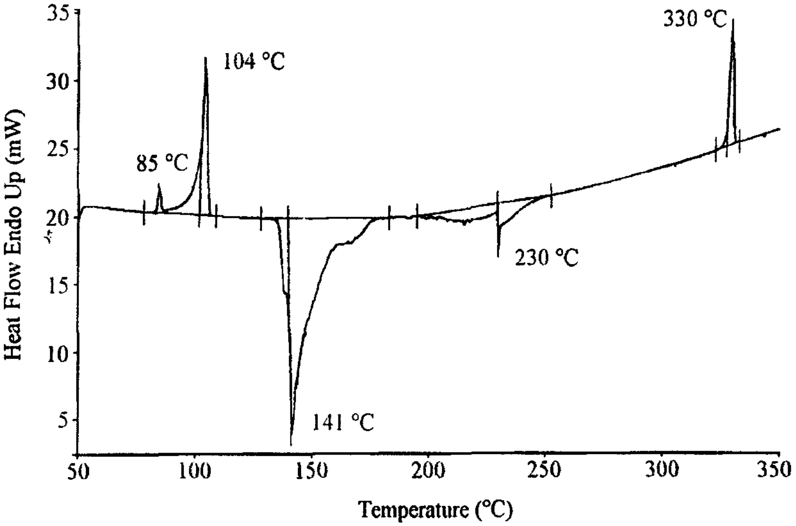

FIGURE 9. DSC Trace of RbDN.

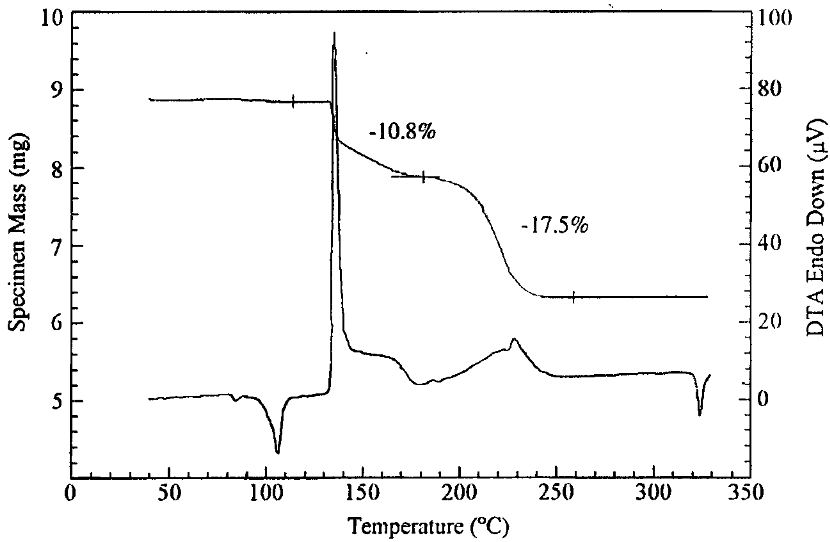

FIGURE 10. TGA Trace of RbDN.

Cesium Dinitramide (CsDN)

The DSC melting point endotherm for CsDN appeared as two overlapping maxima (81 and 86°C) rather than as a discrete peak (Figure 11). Ramping the DSC temperature to 100°C, cooling to ambient and then re-ramping as normal, however, resulted in the loss of the first maxima, possibly due to a loss of occluded recrystallisation solvent molecules. This was supported by hot stage microscopy which showed the evolution of gas from the crystal surface at 82.6°C. Melting of the crystal structure onset at 85.9°C and was complete at 90.6°C. A complex exotherm was seen at 218°C (-209 J/g)[12] with a corresponding 24.0% mass loss by TGA (Figure 12). A mass loss was not observed at the 86°C melting point after thermal annealment of the initial two maxima. A sharp endotherm for the $CsNO_3$ melt was seen at 386°C (+48 J/g, $CsNO_3$ lit.[7] mp 414°C), while the TGA mass loss again showed a stoichiometric decay to the metal nitrate.

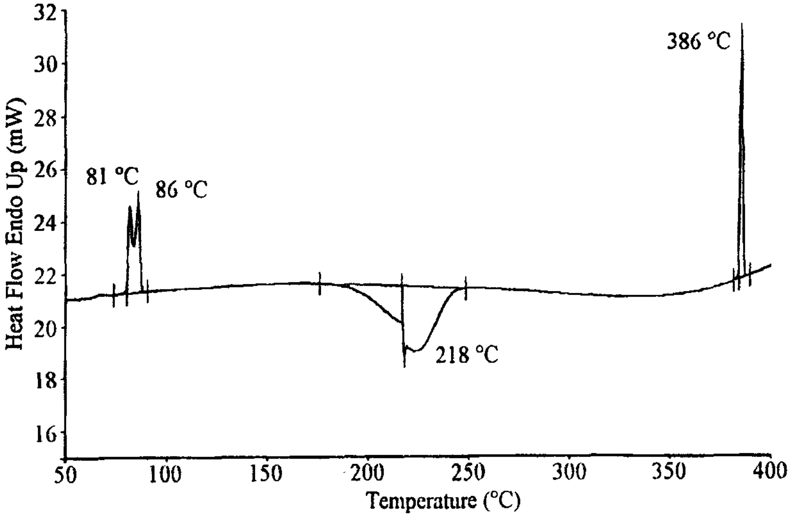

FIGURE 11. DSC Trace of CsDN.

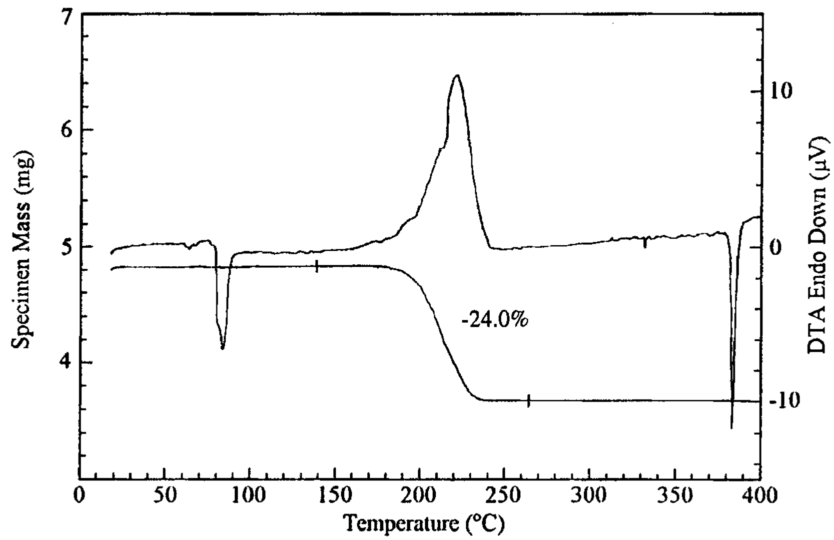

FIGURE 12. TGA Trace of CsDN after annealment of peaks at 81 and 86°C. No mass loss from occluded solvent is observed.

SUMMARY

A summary of the melting points for the dinitramide decomposition products and the corresponding percentage mass losses are presented below (Table). With the exception of LiDN which did not show a melting endotherm for the nitrate, the dinitramide salt residues displayed melting endotherms which approximated the literature values for the corresponding metal nitrates. RbDN unexpectedly gave a melting point 20°C higher than the literature value. A suitable explanation for this is not available at this time. At the completion of each DSC trace for sodium, potassium, rubidium and cesium, the samples were cooled to ambient temperature and then reheated at 5°C/min. A melting endotherm was observed in each case corresponding to the nitrate melt at an identical temperature to that observed in the original trace. No other peaks from the original traces were present. The percentage mass loss measured *via* TGA also matched that expected for the formation of MNO_3 from the dinitramide. Percentage mass loss differences in the range 0.1 - 5.6% were observed between the measured and stoichiometric values.

TABLE. Metal Dinitramide Decomposition Data

MDN	Melting point (MNO_3) (°C)		Mass loss (%)	
	DSC	Literature	TGA	Theoretical
LiDN	-	264	40.2	39.0
NaDN	291	307	38.1	34.1
KDN	319	334	30.2	30.3
RbDN	330	310	28.3	23.0
CsDN	386	414	24.0	18.4

Examination of the DSC traces for all five salts clearly shows that the loss of N_2O with corresponding nitrate formation follows a complex, multi-step mechanism. During their studies on KDN, Dubovitskii *et al*[11] proposed a decomposition scheme based upon evidence gained using ^{15}N labelled substrates. In this five step scheme, radical intermediates were proposed which lead to the formation of the nitrate anion with corresponding N_2O evolution. While this scheme gave a possible pathway for the following thermal decomposition,

$$KN(NO_2)_2 \xrightarrow{\Delta} KNO_3 + N_2O$$

it is clear that this would not apply to all five salts examined here. DSC/TGA traces indicate that NaDN, KDN and RbDN undergo a more complex decomposition route than the lithium and cesium dinitramide salts. It is likely that different thermal decay mechanisms take place for each dinitramide salt and would require separate detailed studies.

In summary, a thermal investigation has been carried out using DSC, TGA, DTA and hot stage microscopy for the Li, Na, K, Rb and Cs dinitramide salt series. The decomposition of each species does not occur by simple internal rearrangement of the dinitramide anion, but rather by a more complex reaction pathway. The probable decomposition products for all five dinitramide salts were the corresponding nitrate salts as evidenced by DSC melting points and TGA mass losses. Further work is currently being carried out in these laboratories on the thermal behaviour of MDN salts and their decomposition products.

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