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Thermal Studies on Rubidium Dinitramide

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ABSTRACT

The present study has been carried out to investigate conflicting reports in the literature on the nature of the thermal decomposition of the energetic oxidant rubidium dinitramide in the liquid state. The techniques employed included DSC, simultaneous TG-DTA, simultaneous TG-mass spectrometry and thermomicroscopy. The measurements were supplemented by quantitative chemical analysis of the reaction products. The results showed that, following fusion at 106 °C, the overall decomposition proceeded in a single exothermic reaction stage forming a mixture of rubidium nitrate and rubidium nitrite in the molar ratio 1.2 : 1.

INTRODUCTION

The thermal properties of the energetic oxidant rubidium dinitramide (RbDN) are of interest due to its potential use in pyrotechnics. To date only limited studies have been carried out on this material. DSC studies by Babkin *et al* [1] showed that rubidium dinitramide melted at 108 °C and when mixed with $RbNO_3$ formed a eutectic at 84.5 °C. The rate of decomposition of the dinitramide in vacuum was found to decrease markedly at temperatures above the eutectic point.

Cliff & Smith [2] obtained similar results in their DSC studies and reported a small endothermic peak at 85 °C and the melting of the sample at 104 °C. A two stage exothermic decomposition reaction was observed with peaks at 141 °C and 230 °C. TG-DTA studies showed that these exothermic peaks were accompanied by mass losses of 10.8% and 17.5%, respectively. The measured overall mass loss of 28.3% was compared with the theoretical value of 23.0% based on conversion to $RbNO_3$ as shown by the equation: $RbN(NO_2)_2 \rightarrow RbNO_3 + N_2O$. In addition, Cliff and Smith [3] in an X-ray diffraction study of the decomposition products of five alkali metal dinitramides identified only the alkali metal nitrates.

In contrast, Berger *et al* [4] found from DSC and TG studies that the melting peak for rubidium dinitramide at 106 °C was followed by a single stage exothermic decomposition reaction with a peak maximum at 234 °C. Both $RbNO_2$ and $RbNO_3$ were found to be formed in the decomposition process.

In order to resolve these conflicting observations a programme of work has been carried out to investigate further the thermal decomposition of rubidium dinitramide. The emphasis has been placed on decomposition in the liquid state and follows a similar study on potassium dinitramide [5].

EXPERIMENTAL

Sample Preparation

Rubidium dinitramide was prepared by the addition of rubidium hydroxide to ammonium dinitramide. The resulting product was recrystallised in methanol yielding crystalline white needles. Measurements have been carried out on the sample as prepared and on a portion that had been crushed and passed through a 150 µm sieve. Care was taken to minimise the exposure of the samples to ambient light on handling and to store in darkened bottles in a desiccator.

Thermal Analysis Experiments

Preliminary thermomicroscopy experiments were performed under reflected light conditions using a modified Stanton Redcroft HSM5 hot stage unit. The samples were heated at 10 °C min^{-1} in alumina crucibles, in an argon atmosphere, using a sample mass of 2.5 mg. It was observed that, as in the case of potassium dinitramide [5], the fusion of rubidium dinitramide, was followed by a vigorous bubbling decomposition reaction.

Therefore encapsulated aluminium crucibles were employed for the DSC and TG-DTA experiments in order to reduce the loss of the sample through spitting and a pin-hole was inserted in the crucible lid to permit the escape of gaseous reaction products. The measurements were carried out in an argon atmosphere at a heating rate of 10 °C min^{-1} using a sample mass of 2.5 mg. The DSC studies were performed using a Mettler-Toledo DSC 822[e] and the simultaneous TG-DTA measurements were carried out with a Mettler- Toledo SDTA 851[e].

Simultaneous TG-mass spectrometry experiments were performed using a Du Pont TG-951 thermobalance linked to a VG Gas Analysis Gaslab 300 quadrupole mass spectrometer via a molecular leak interface and heated capillary. The experiments were carried out by heating 5 mg samples in alumina crucibles, fitted with alumina lids with pinholes, at 10 °C min^{-1} in an argon atmosphere.

Quantitative Analysis of Reaction Products

The nitrate content of the decomposition products of rubidium dinitramide was determined using an ion selective electrode. Since nitrite interferes with the measurements it was removed by the addition of sulphamic acid. It was not possible to analyse partially decomposed rubidium dinitramide samples by this technique since the presence of dinitramide was found to interfere with the analysis. The nitrite content of the decomposed rubidium dinitramide was measured using a spectrophotometric method. This was based on the diazotisation of sulphanilamide by the nitrite ion in acid solution, followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride.

RESULTS AND DISCUSSION

Thermal Analysis Studies

DSC studies on rubidium dinitramide in both crystal and powder form showed that, following the fusion peak at 107 °C, an exothermic decomposition reaction was given with overlapping peaks at 230 °C and 239 °C. A representative curve is shown in Fig. 1 and the extrapolated onset (T_e) and peak (T_p) temperatures for the samples are given in Table 1. The results showed good reproducibility, in spite of the bubbling nature of the reaction, and indicated that there were no significant differences between the two dinitramide samples.

Table 1

DSC Temperatures for Rubidium Dinitramide Fusion and Decomposition

Form	Fusion		Decomposition			
	T_e / °C	T_p / °C	T_e / °C	T_p1 / °C	T_p2* / °C	T_p3 / °C
Crystals	106.4	107.1	199.8	230.4	238.2	239.4
	± 0.0	± 0.0	± 0.3	± 0.1	± 0.1	± 0.1
Powder	106.3	107.0	199.3	230.4	238.0	239.2
	± 0.1	± 0.0	± 0.4	± 0.3	± 0.1	± 0.2

*peak minimum

Thermomicroscopy studies showed that the apparent dip on the DSC curves, which occurred at 238 °C, was associated with the onset of formation of a white solid in the melt. This behaviour was also observed for potassium dinitramide [5]. In both cases it is considered that a peak corresponding to the exothermic heat of recrystallisation of the reaction products was superimposed on the main decomposition exotherm, thus giving rise to the two exothermic peaks. DSC curves for the decomposition of rubidium and potassium dinitramides are compared in Fig. 2 and the similarity of the two curves indicates that the metal cation does not appear to influence the decomposition of the dinitramide anion in the liquid state.

The enlarged DSC plot for rubidium dinitramide in Fig. 3 shows that, in addition to the melting peak, there was a very small peak at 92 °C. This peak, which we have observed in both crystal and powder forms, is considered to be due to the melting of an ammonium dinitramide trace impurity. DSC measurements on a 50% RbDN-50% $RbNO_3$ mixture (Fig. 3) have confirmed the value of 84.5 °C reported by Babkin *et al*. [l] for the RbDN-$RbNO_3$ eutectic temperature.

A simultaneous TG-DTA curve for the rubidium dinitramide in crystal form is given in Fig. 4 and confirmed that the main decomposition reaction took place in a single stage. It can be seen from the expanded plot in Fig. 5 that there was also a small mass loss (~0.1%) starting in the region of 90 °C, which was slowed by the fusion of the dinitramide. The mass losses for both crystal and powder forms are summarised in Table 2. The mean value for the overall mass loss was of 26.7%.

Table 2

Mass Losses for Rubidium Dinitramide Decomposition

Form	Mass loss / %		
	Solid	Liquid	Total
Crystals	0.13	26.52	26.65
	± 0.01	± 0.16	± 0.18
Powder	0.08	26.58	26.66
	± 0.02	± 0.01	± 0.01

Simultaneous TG-MS studies showed that the gaseous products of decomposition in the liquid state were N_2O and NO and a typical plot is shown in Fig. 6. Experiments were also carried out using a gauze lid in place of the alumina lid and similar results were obtained. This indicated that the presence of a self-generated atmosphere of product gases did not appear to have a significant influence on the decomposition mechanism.

Analysis of Reaction Products

FTIR spectroscopy showed that both rubidium nitrite and rubidium nitrate were formed in the decomposition of rubidium dinitramide, thus confirming the earlier work of Berger *et al* [4]. A number of completely decomposed samples of rubidium dinitramide from both DSC and TG experiments were analysed quantitatively for nitrate and nitrite content. The results, which showed good reproducibility, are summarised in Table 3. The mean values for rubidium nitrate and rubidium nitrite content of 57% and 43%, respectively indicate that the molar ratio of rubidium nitrate to rubidium nitrite is 1.2 : 1. This compares with a value for potassium dinitramide of 1.3 : 1 obtained under the same conditions, indicating a small increase in the amount of nitrite formed by the decomposition of the rubidium salt.

Table 3

Analysis of Completely Decomposed Samples of Rubidium Dinitramide for $RbNO_3$ and $RbNO_2$ Content

Technique	Mass / mg	Crucible	$RbNO_3$ / %	$RbNO_2$ / %
TG	5	alumina	57.7± 0.3	42.5 ± 0.0
DSC	2.5	aluminium	56.0 ± 0.5	43.8 ± 0.4
		Mean	56.8 ± 1.1	43.2 ± 0.8

CONCLUSIONS

Rubidium dinitramide was found to melt at 106 °C and to decompose exothermically in a single stage reaction which was accompanied by vigorous bubbling. The gaseous products of decomposition were found by simultaneous TG-MS to be N_2O and NO and these studies showed that the decomposition did not appear to be influenced by the presence of self-generated atmosphere effects. Thermomicroscopy studies enabled the second exothermic peak observed in DSC experiments to be attributed to the re-crystallisation of the products of decomposition from the melt. The DSC peak temperatures were similar to those obtained previously for potassium dinitramide and suggest that the metal cation does not have a significant influence of the thermal stability in the liquid state. Both rubidium nitrate and nitrite were formed in the decomposition reaction and quantitative chemical analysis gave a molar ratio of rubidium nitrate to rubidium nitrite of 1.2 : 1.

Further work is now in progress to investigate the decomposition of rubidium dinitramide in the liquid state in more detail and also to characterise the behaviour of the material in the solid state. The latter studies will include the effect of exposure to artificial daylight and to UV light. Measurements are also being carried out on a second sample of rubidium dinitramide which has been found to exhibit an additional exothermic decomposition reaction in the region of 170°C.

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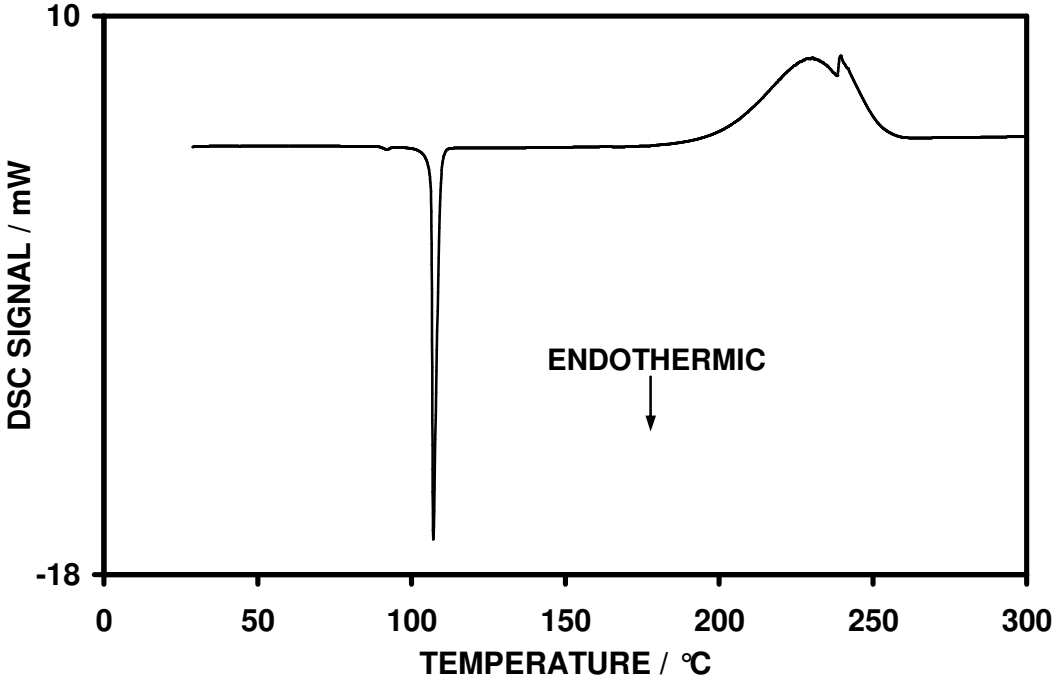

FIG. 1. DSC CURVE FOR RUBIDIUM DINITRAMIDE
(Sample mass, 2.5 mg; heating rate, 10 ℃ min^{-1}; atmosphere, argon)

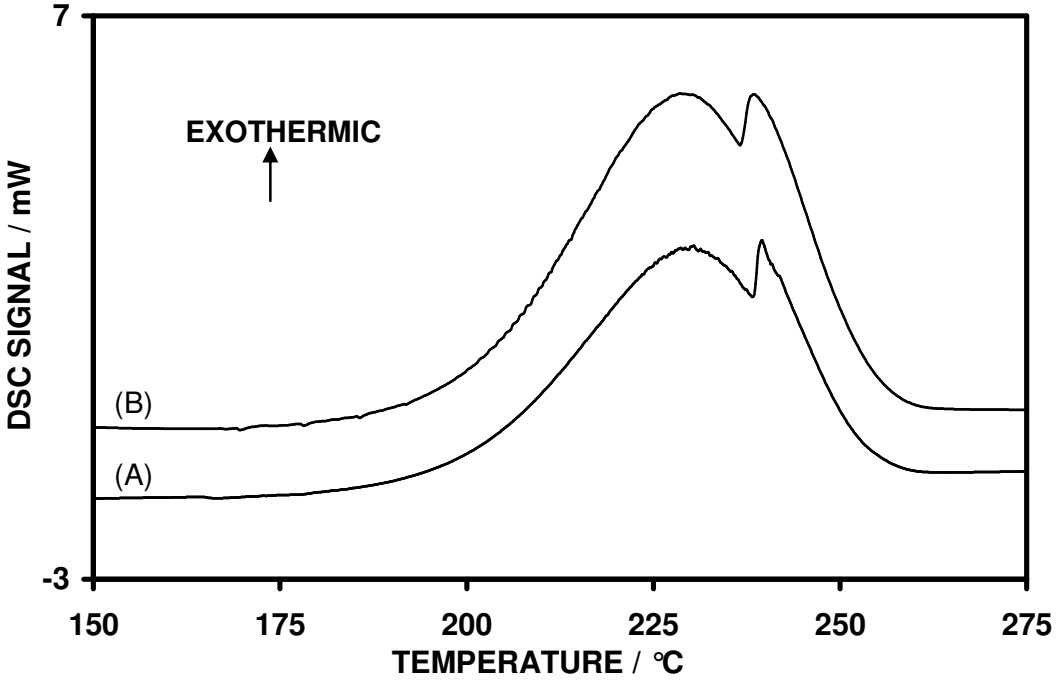

FIG. 2. DSC CURVES COMPARING THE DECOMPOSITION OF (A) RUBIDIUM DINITRAMIDE AND (B) POTASSIUM DINITRAMIDE
(Sample mass, 2.5 mg; heating rate, 10 ℃ min^{-1}; atmosphere, argon)

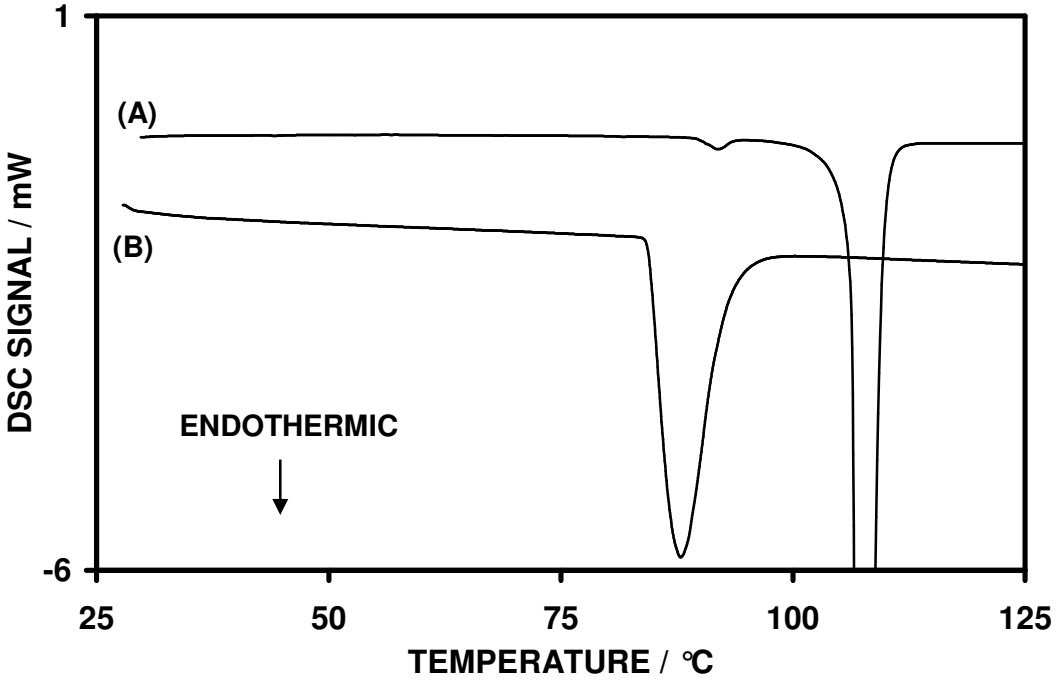

FIG. 3. DSC CURVES FOR (A) RbDN (2.5 mg) AND (B) A 50% RbDN-50% $RbNO_3$ MIXTURE (5 mg)
(Heating rate, 10 °C min^{-1}; atmosphere, argon)

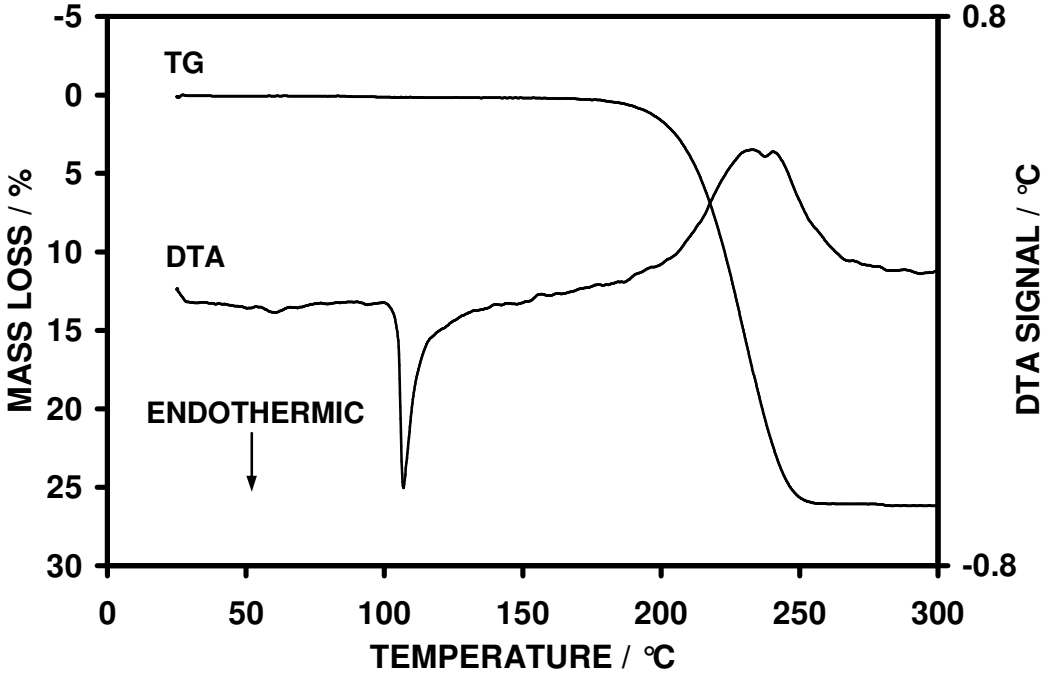

FIG. 4. TG-DTA CURVES FOR RUBIDIUM DINITRAMIDE
(Sample mass, 2.5 mg; heating rate, 10 °C min^{-1}; atmosphere, argon)

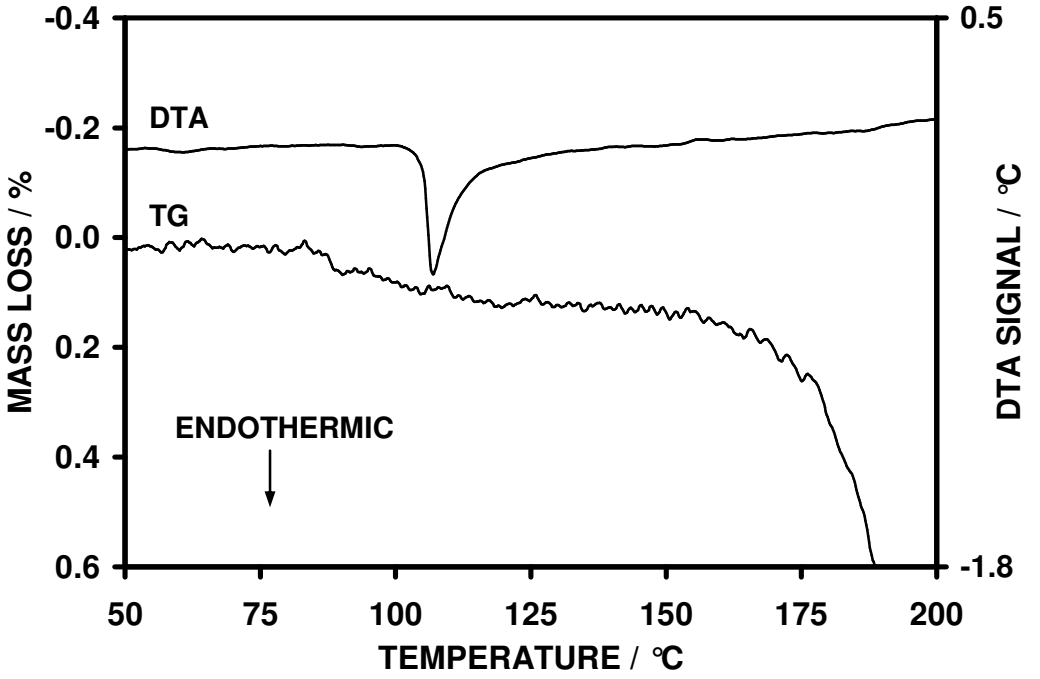

FIG. 5. EXPANDED TG-DTA CURVES FOR RUBIDIUM DINITRAMIDE
(Sample mass, 2.5 mg; heating rate, 10 °C min^{-1}; atmosphere, argon)

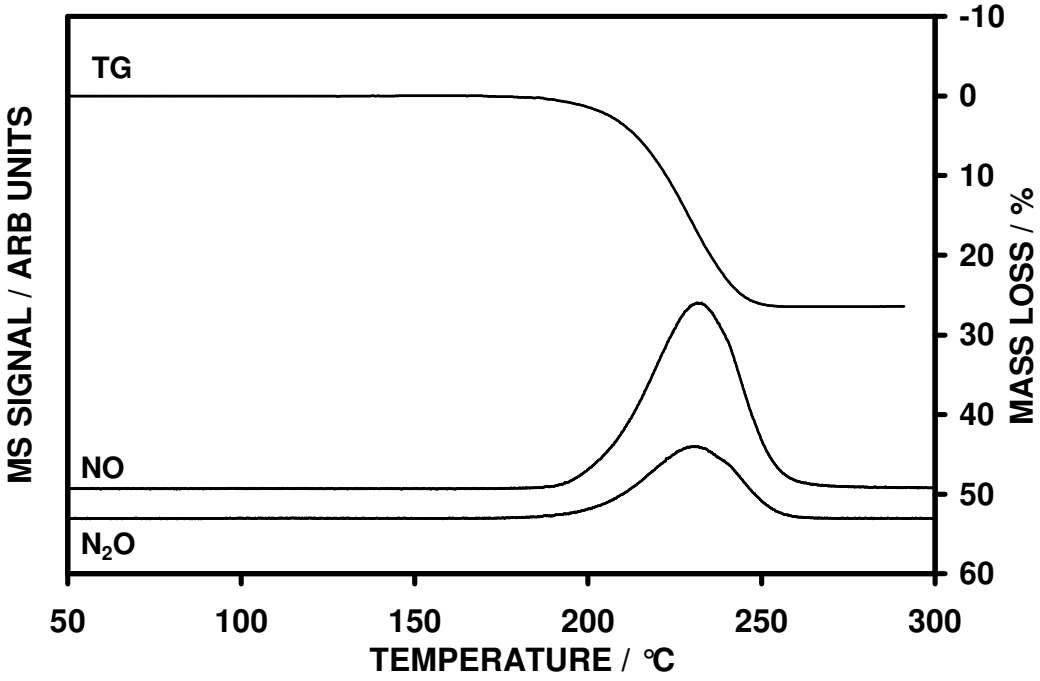

FIG. 6. TG-MS CURVES FOR RUBIDIUM DINITRAMIDE
(Sample mass, 5 mg; heating rate, 10 °C min^{-1}; atmosphere, argon)