Journal of Thermal Analysis, Vol. 38 (1992) 641-648

PRELIMINARY STUDIES ON THE TITANIUM-SODIUM NITRATE-ALLOPRENE PYROTECHNIC SYSTEM

E. L. Charsley, S. B. Warrington, P. Emmott, T. T. Griffiths* and J. Queay**

THERMAL ANALYSIS CONSULTANCY SERVICE, LEEDS POLYTECHNIC, CALVERLEY STREET, LEEDS, LS1 3HE, U.K.
*DEFENCE RESEARCH AGENCY (MILITARY DIVISION), FORT HALSTEAD, SEVENOAKS, KENT, TN14 7BP, U.K.

Simultaneous TG-DTA-MS and TG-DSC have been used to investigate the complex reaction which takes place in the region of 300°C when the chlorinated rubber Alloprene is added to pyrotechnic compositions containing equal parts by weight of titanium and sodium nitrate. The results have been compared with those obtained for the titanium-strontium nitrate-Alloprene system.

Keywords: pyrotechnic system, titanium-sodium nitrate-alloprene, simultaneous TG-DTA-MS and TG-DSC

Introduction

Previous work has shown that organic binders play an important part in the chemical reactions of pyrotechnic systems based on mixtures of magnesium or titanium with sodium or strontium nitrate [1, 2]. The studies were carried out with a wide range of binders incorporated at the 2% to 12% level. The addition of a binder was found to influence the performance characteristics of burn rate, light output and ignition temperature of these tracer compositions. Thermal analysis studies showed that additional pre-ignition exothermic reactions were introduced into the DTA curves of the compositions containing binders. The magnitude of these exothermic reactions changed with binder concentration and could result in ignition taking place at lower a temperature exotherm [3].

A programme of work has commenced recently to investigate the chemical role of binders in pyrotechnic compositions using simultaneous TG-MS and TG-DTA-MS. A preliminary study by TG-MS on the titanium-strontium nitrate sys-

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

tem containing the chlorinated rubber Alloprene, revealed an overlapping series of exothermic reactions over the temperature range 300° to 700°C [4]. Simultaneous TG-DTA-MS was used to carry out a more detailed investigation of the complex reaction which takes place between strontium nitrate and Alloprene in the region of 300°C [5]. The following reaction sequence was proposed:

a) The decomposition of Alloprene to produce HCl.

b) The reaction of part of the HCl with $Sr(NO_3)_2$ to give $SrCl_2$, NO_2, O_2 and H_2O.

c) Oxidation of part of the carbonaceous Alloprene residue by the oxidising gases produced in (b) to form CO_2.

The extent of reaction was found to be increased by the presence of titanium which prevented shrinkage of the mixtures, due to partial fusion of the Alloprene during decomposition, thus allowing increased gas-solid interaction.

In the present work the corresponding reaction in the region of 300°C has been investigated for the titanium-sodium nitrate-Alloprene system and the results compared with those obtained for the strontium nitrate system.

Experimental

The specification of the ingredients has been given elsewhere [6]. Compositions containing equal parts by weight of titanium and sodium nitrate with 0–12% Alloprene were prepared by dry blending.

Simultaneous TG-DTA-MS studies were carried out using a Stanton Redcroft STA 1500 TG-DTA unit linked to 300 amu range VG quadrupole mass spectrometer through a molecular leak interface [7]. TG-DSC studies were performed using a Stanton Redcroft 625 unit. In both cases the experiments were carried out in an argon atmosphere heating 20 mg samples, in alumina crucibles with loose fitting platinum lids, at 10 deg·min^{-1}. The results were supplemented by thermomicroscopy and by chloride analysis using a specific-ion electrode.

Results

TG-DSC studies confirmed that the reaction in the titanium-sodium nitrate-Alloprene system in the region of 300°C was exothermic in nature and showed that the exothermicity increased with increasing Alloprene content. Superimposed on this exothermic reaction were endothermic peaks due to the solid-solid transition and fusion of sodium nitrate at 276° and 308°C respectively. This is

illustrated in Fig. 1 for compositions containing 0% to 12% Alloprene. The temperature range of the exothermic reaction can be seen to be essentially independent of Alloprene concentration. The reduction in temperature of the nitrate fusion peaks shown by the compositions containing Alloprene was found to be due to the presence of sodium chloride formed in the pre-fusion region.

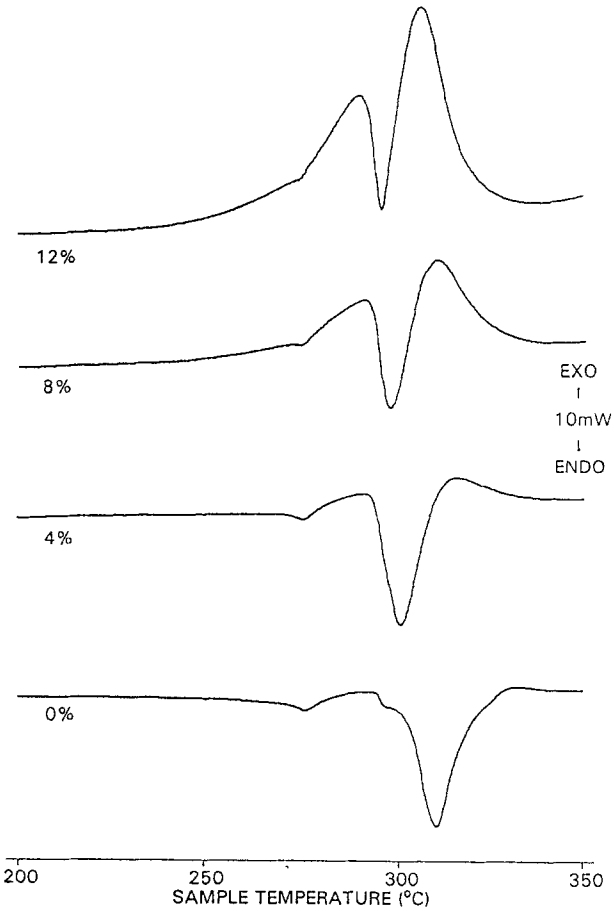

Fig. 1 DSC curves for titanium-sodium nitrate-Alloprene composition containing 0–12% Alloprene (20 mg sample weight, 10 deg·min^{-1} heating rate, argon atmosphere)

The overall weight loss associated with the first reaction stage increased in a linear manner as the Alloprene content was increased. The values ranged from 1.8% to 12.9% for compositions containing from 2% to 12% Alloprene.

These losses were greater than those observed for the corresponding titanium-strontium nitrate-Alloprene compositions where losses of 1.8% to 10.8%

were given. This is illustrated in Fig. 2 which shows the TG-DSC curves for the titanium-sodium nitrate and titanium-strontium compositions containing 12% Alloprene. Comparison of the DSC curves shows that the reaction in the sodium nitrate system was considerably more exothermic than that in the strontium nitrate system.

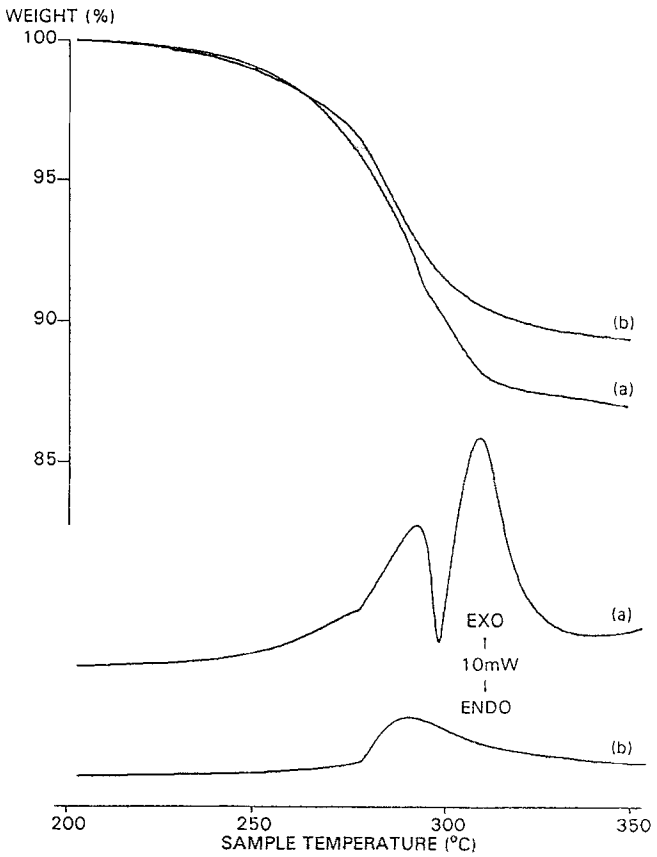

Fig. 2 TG-DSC curves for titanium-sodium nitrate and titanium-strontium nitrate compositions containing 12% Alloprene (20 mg sample weight, 10 deg·min^{-1} heating rate, argon atmosphere)

The importance of self-generated atmosphere effects was demonstrated for the ternary strontium nitrate compositions where the extent of reaction was markedly reduced in the absence of a crucible lid [5]. TG-DSC experiments carried out on the titanium-sodium nitrate composition containing 12% Alloprene, without a lid, showed that the effect was considerably less marked in this system.

TG-DTA-MS studies revealed that, as for the titanium-strontium nitrate-Alloprene system, the main gaseous reaction products were NO, CO_2, H_2O together with some N_2. The EGA profiles for NO and CO_2, for the composition containing 12% Alloprene, are shown in Fig. 3 together with the TG and DTA plots. The spikes on the EGA traces were shown by thermomicroscopy to be due to the vigorous bubbling nature of the reaction following fusion of the nitrate in the region of 300°C. It can be seen that a major part of the exothermic reaction takes place in the latter stages of the weight loss and this is accompanied by a large part of the CO_2 evolution.

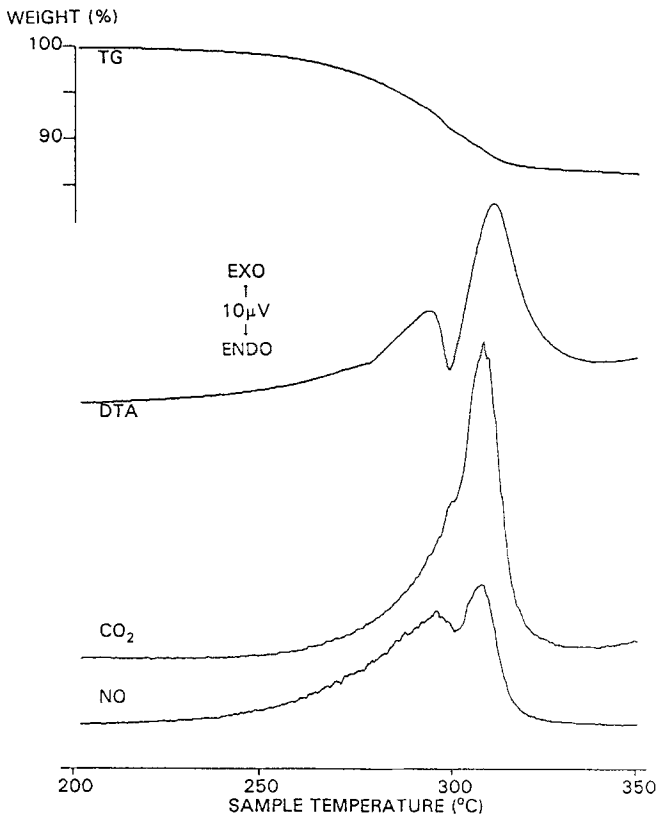

Fig. 3 TG-DTA-MS curves for a 44% titanium-44% sodium nitrate-12% Alloprene composition (20 mg sample weight, 10 deg·min^{-1} heating rate, argon atmosphere)

Semi-quantitative TG-DTA-MS studies, using sodium bicarbonate as an internal standard, showed that for 20 mg of the titanium-sodium nitrate compositions containing 12% Alloprene approximately 0.55±0.05 mg of CO_2 were

released. This is considerably higher than the figure of 0.22±0.02 mg measured for the corresponding composition containing strontium nitrate.

The reduced influence of the self-generated atmosphere effects on the sodium nitrate compositions, noted in the TG-DSC work, were confirmed by the MS studies. This is illustrated in Fig. 4 which shows the CO_2 profiles, for experiments performed with and without crucible lids, for the ternary sodium and strontium nitrate compositions containing 12% Alloprene.

Comparison of the results for the ternary sodium nitrate system with those obtained for sodium nitrate-Alloprene mixtures indicated that, unlike the strontium nitrate system, the extent of reaction was not significantly influenced by the presence of titanium.

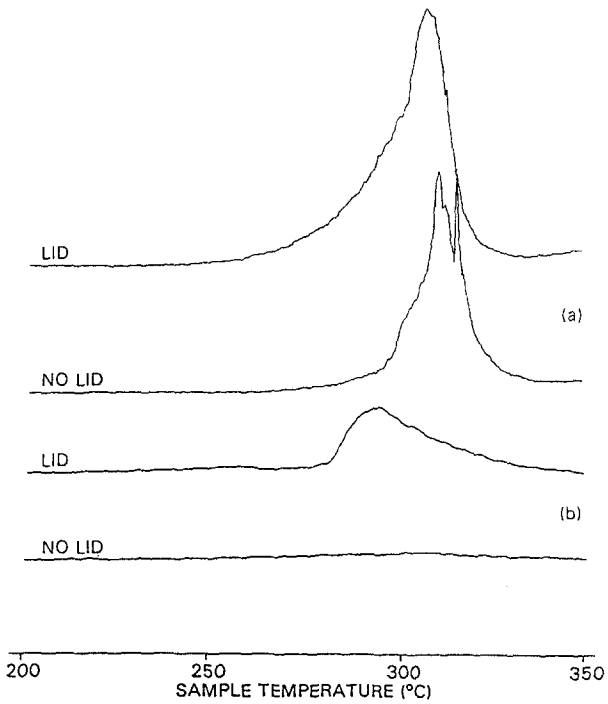

Fig. 4 CO_2 profiles showing self-generated atmosphere effects for a) titanium-sodium nitrate and b) titanium-strontium nitrate compositions containing 12% Alloprene (20 mg sample weight, 10 deg·min^{-1} heating rate, argon atmosphere)

Chloride analysis of a range of titanium-sodium nitrate-Alloprene residues from the first reaction stage showed that over 90% of the HCl from the Alloprene was retained. This compared with values in the range 60–70% obtained for the compositions containing strontium nitrate.

Discussion

The measured weight losses for the sodium nitrate compositions (after correction for carbon loss) were found to be in reasonable agreement with those calculated for the reaction:

$$2NaNO_3+2HCl \rightarrow 2NaCl+2NO_2+1/2O_2+H_2O$$

$$NO_2 \leftrightarrows NO+1/2O_2$$

This indicated that most of the HCl evolved from the Alloprene had reacted with the nitrate and this was supported by the chloride analysis results. This was in contrast to the strontium nitrate compositions where lower weight losses were given and chloride analysis showed that only 60–70% of the HCl was retained.

Previous work on the titanium-strontium nitrate-Alloprene compositions had shown that the exothermic nature of the first reaction stage was due to oxidation of the carbonaceous Alloprene residue, since the reaction of strontium nitrate with HCl reaction was endothermic [5]. It has been shown that a marked increase in the exothermicity of reaction was given on replacing strontium nitrate with sodium nitrate. This increase in reaction was confirmed by semi-quantitative MS measurements of CO_2 on compositions containing 12% Alloprene. It was found that approximately 21% of the total carbon in the Alloprene, based on the empirical formula $(C_{10}H_{11}Cl_7)_n$, was oxidised in the sodium nitrate composition compared with 8% for the strontium nitrate composition. The oxidation reaction was considered to proceed by the following route:

$$3/2C+2NO_2+1/2O_2 \rightarrow 3/2CO_2+2NO$$

$$C+2NO \rightarrow CO_2+N_2$$

From the experiments carried out to date, the presence of titanium appeared to have little effect on the reaction between sodium nitrate and Alloprene, in contrast to the increase in reaction observed in the strontium nitrate system.

In the case of the strontium nitrate system, the extent of reaction was also markedly influenced by self-generated atmosphere effects and reaction was considerably reduced in the absence of a crucible lid. This effect was found to be less marked for the sodium nitrate system, where the bulk of the reaction took place in the fused state under the experimental conditions used.

Conclusions

It has been shown that sodium nitrate undergoes a similar complex reaction with Alloprene, in the region of 300°C, to that given by strontium nitrate. The sodium nitrate system showed a higher degree of reactivity and was less influenced by either the presence of titanium or by self-generated atmosphere effects.

References

1 T. T. Griffiths, E. L. Charsley and J. A. Hider, Proc. 3 Congrès International de Pyrotechnie Spatiale et 12th International Pyrotechnic Seminar, Association Francaise de Pyrotechnie, 1987, p. 397.
2 T. T. Griffiths, E. L. Charsley and J. A. Hider, Proc. of the 13th International Pyrotechnics Seminar, IIT Research Institute, Chicago 1988, p. 393.
3 E. L. Charsley, J. A. Hider, T. J. Barton and T. T. Griffiths, Thermal Analysis, Vol. 2, Ed. B. Miller, Wiley Heyden, 1982, p. 1440.
4 T. T. Griffiths, J. Queay, E. L. Charsley and S. B. Warrington, Proc. of the 15th International Pyrotechnics Seminar, IIT Research Institute, Chicago 1990, p. 353.
5 P. Emmott, T. T. Griffiths, J. Queay, E. L. Charsley and S. B. Warrington, Proc. of the 16th International Pyrotechnics Seminar, Sweden, 1991, in press.
6 P. Emmott, T. T. Griffiths, J. Queay, E. L. Charsley and S. B. Warrington, Proc. of the 17th International Pyrotechnics Seminar, China, 1991, in press.
7 E. L. Charsley, S. B. Warrington, T. T. Griffiths and J. Queay, Proc. of the 14th Interantional Pyrotechnics Seminar, Jersey, RARDE, 1989, p. 763.

Zusammenfassung — Zur Untersuchung der im Bereich um 300°C eintretenden komplexen Reaktion bei Zusatz des chloriertem Kautschuks Alloprene zu pyrotechnischen Gemischen aus Titan und Natriumnitrat wurden simultane TG-DTA-MS und TG-DSC angewendet. Die Ergebnisse wurden mit denen verglichen, die man im System Titan-Strontiumnitrat-Alloprene erhielt.