

THERMAL ANALYSIS STUDIES ON THE BORON-POTASSIUM PERCHLORATE-NITROCELLULOSE PYROTECHNIC SYSTEM

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Abstract

Studies have been carried out on the boron-potassium perchlorate-nitrocellulose pyrotechnic system by DSC, simultaneous TG-DTA-mass spectrometry and chemical analysis. Quantitative measurements have been made on the exothermic pre-ignition reaction which took place above 360°C and the results have been compared with those obtained previously for the corresponding systems containing zirconium and a zirconium/nickel alloy.

Keywords: boron-potassium perchlorate-nitrocellulose system, pyrotechnic system, TG-DTA-MS

Introduction

Previous studies on the zirconium-potassium perchlorate-nitrocellulose (NC) pyrotechnic system, using simultaneous thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS), showed that zirconium and potassium perchlorate gave an exothermic solid state reaction starting in the region of 400°C, which overlapped with the decomposition of unreacted potassium perchlorate at a higher temperature [1]. Quantitative measurements were made on this solid state reaction by differential scanning calorimetry (DSC) and by chemical analysis using ion-specific electrodes (ISE) to measure potassium perchlorate and chloride contents of the reaction products [2]. DSC was shown to be an excellent method for the quantitative determination of the amount of perchlorate reacted. A similar experimental approach was used in the study of the corresponding system containing a zirconium/nickel alloy [3].

In the present work, results are reported for studies on the boron-potassium perchlorate-nitrocellulose system. The results are compared with those obtained for the corresponding zirconium and zirconium/nickel systems.

Experimental

Compositions were prepared from boron (H.C.Starck, purity 92%, particle size 0.5 μm as measured by a Fisher sub-sieve sizer) and potassium perchlorate (particle size < 60 μm , purity 99%). The nitrocellulose was type 220 E, with a nitrogen content of 12.1%. The compositions were prepared in a Turbula mixer before granulation by the addition of 1% by weight of nitrocellulose (dissolved in an ethanol/acetone mixture) to give a grain size of about 0.5 mm.

DSC experiments were carried out using a DuPont 9900 unit and a high temperature unit developed for pyrotechnic studies [4]. Simultaneous TG-DTA-MS work was performed using a Stanton Redcroft STA 1500 interfaced to a VG Micro-mass quadrupole mass spectrometer. Thermomicroscopy experiments were carried out using a system based on a Stanton Redcroft HSM-5 hot stage unit [5]. The measurements were carried out in purified argon or helium, where possible using zirconium powder as an internal oxygen getter.

Analyses of reaction products, prepared by heating a composition to different temperatures in the DuPont DSC apparatus, for perchlorate and chloride content were performed using DSC and a chloride ion-specific electrode (ISE) respectively. Full details of the experimental procedure has been given previously [2].

Results

Preliminary thermal analysis studies

The thermal behaviour of potassium perchlorate and nitrocellulose has been reported earlier [1]. The oxidative behaviour of the boron was studied by simultaneous TG-DTA in air and the results are shown in Fig. 1. A mass loss of about 3.3% was observed on heating to 350°C. This was followed by the main oxidation reaction which started at about 500°C and accelerated rapidly above 650°C. The overall mass gain of approximately 125% was essentially completed in the region of

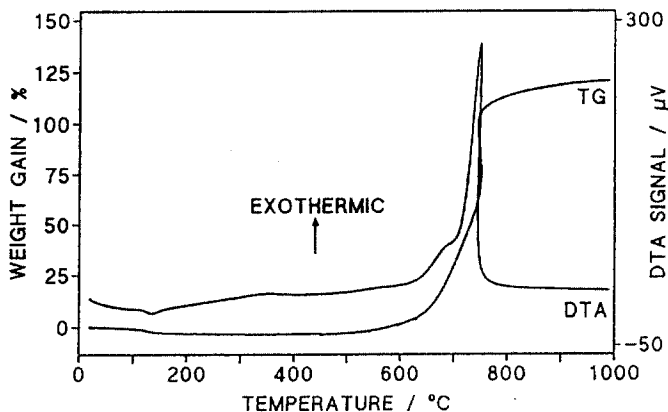


Fig. 1 Simultaneous TG-DTA curves for the oxidation of boron (sample weight 5 mg; heating rate 10°C min⁻¹; atmosphere: air)

1000°C. The boron was therefore be seen to be considerably less reactive with respect to aerial oxidation than either the zirconium or zirconium/nickel alloy samples where the major part of the oxidation reaction took place below 500°C.

Measurements on the boron, by simultaneous TG-DTA-mass spectrometry in a helium atmosphere, showed that the initial mass loss was due to the evolution of water and a further water loss of about 1.4% was observed on heating to 600°C. The ability of boron to retain water to high temperatures has been seen in earlier work on samples of amorphous boron [6].

Before carrying out quantitative measurements on the extent of reaction, a preliminary series of experiments was carried out on the high-temperature DSC unit to determine the conditions required for non-ignition studies. Although the sample weight was limited to 5 mg, an ignition reaction was given for the compositions containing more than 10% boron. The ignition temperature was found to be independent of boron content and a mean value of $548 \pm 1^\circ\text{C}$ was obtained for compositions containing from 17.5–60% boron.

Curves for the compositions containing 20, 40 and 60% boron are shown in Fig. 2. As was observed for the zirconium and zirconium/nickel alloy based systems, the small exotherm corresponding to the decomposition of nitrocellulose at about 200°C, was followed by the endothermic solid-solid transition of potassium perchlorate at about 300°C. However, in contrast to these systems, where the main exothermic reaction had taken place in the region of 450°C, the boron compositions showed only a low energy pre-ignition reaction which started about 350°C and overlapped with the main reaction exotherm. The magnitude of this pre-ignition reaction increased with increasing boron content. Similar results were obtained in a preliminary study on this system [7]. The DSC curves for the 40% boron and zirconium systems are shown in Fig. 3 and illustrate the marked reduction in exothermicity in the former case.

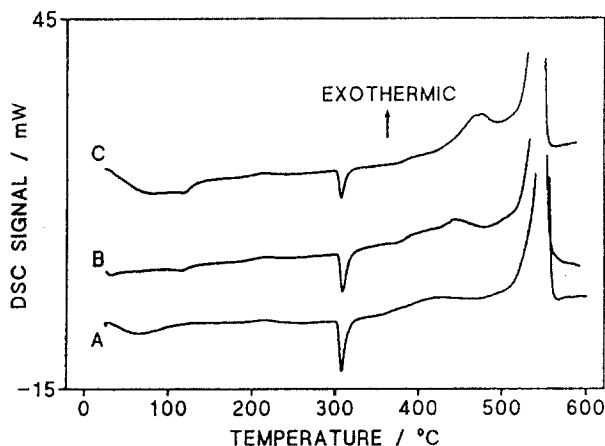


Fig. 2 DSC curves for a) 20% B-79% KClO_4 -1% NC, b) 40% B-59% KClO_4 -1% NC and c) 60% B-39% KClO_4 -1% NC compositions (sample weight 5 mg; heating rate $10^\circ\text{C min}^{-1}$; atmosphere: argon)

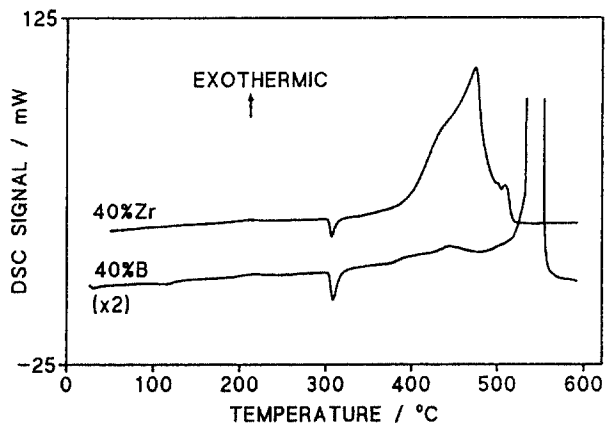


Fig. 3 DSC curves for 40% B-59% KClO_4 -1% NC and 40% Zr-59% KClO_4 -1% NC compositions (sample weight 5 mg; heating rate 5°C min^{-1} ; atmosphere: argon)

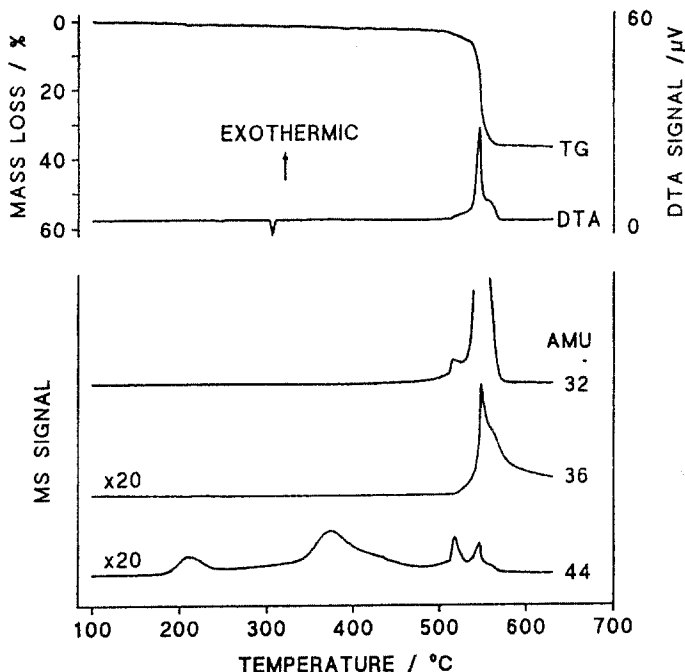


Fig. 4 TG-DTA-MS curves for a 10% B-89% KClO_4 -1% NC composition (sample weight 10 mg; heating rate $10^\circ\text{C min}^{-1}$; atmosphere: helium)

Simultaneous TG-DTA-mass spectrometry on the composition containing 10% boron (Fig. 4) showed that the main gaseous product given on heating was oxygen, which was evolved rapidly above the melting temperature of the KClO_4 - KCl eutectic in the region of 505°C . This is attributed to the decomposition of unreacted po-

tassium perchlorate. The curve for carbon dioxide showed a peak at 210°C, due to the decomposition of the nitrocellulose, followed by a broad asymmetrical peak with a maximum at 374°C, which resulted from the reaction between the carbonaceous residue from the nitrocellulose decomposition and potassium perchlorate [8]. Smaller, irregular peaks were seen at higher temperatures, the first starting sharply in the region of the KClO_4 -KCl eutectic melting point.

There appeared to be very small responses for ions at 51, 67, and 70 amu, corresponding possibly to ClO , ClO_2 and Cl_2 , leading to broad peaks centred around 350°C. These ions also gave small sharp peaks during the main perchlorate decomposition stage, above 500°C. These peaks were accompanied by much larger peaks for ions in the 35–38 amu range, which indicated that hydrogen chloride was being evolved.

Thermomicroscopy studies on the 10% B composition showed no evidence of the KClO_4 -KCl eutectic melting in the region of 505°C. Melting was first observed to begin slowly in the region of 520°C and to become rapid above 540°C. This is shown in the sequence of video prints in Fig. 5. It can be seen that the boron particles have aggregated together in clumps and do not appear to be completely wetted by the decomposing perchlorate. This is in contrast to the results observed for the zirconium and zirconium/nickel systems.

Observations on compositions containing from 20–60% boron, made under the same conditions as the preliminary DSC experiments showed the appearance of a

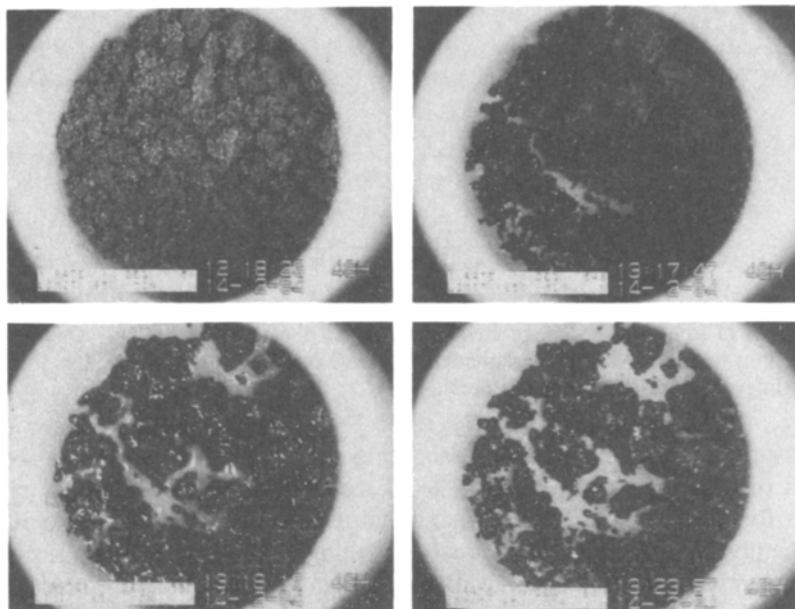


Fig. 5 Video prints showing the reaction of a 10% B-89% KClO_4 -1% NC composition. Top left, 50°C; top right, 548°C; bottom left, 557°C, bottom right, 600°C (sample weight 5 mg; heating rate 10°C min⁻¹; atmosphere: helium)

liquid phase in the region of 550°C. This is presumed to be due to the fusion of unreacted perchlorate, promoted by the reaction products, and it is considered that this could be the trigger for the ignition reaction.

Quantitative measurements on the pre-ignition reaction

A series of experiments was carried out on the DuPont 9900 DSC to investigate the influence of composition on the extent of reaction for compositions containing 0–60% boron. In view of the reduced extent of the solid state reaction between boron and potassium perchlorate compared with the zirconium and zirconium/nickel systems, a maximum temperature of 470°C was chosen, rather than the value of 420°C used previously, in order to increase the amount of reaction. The samples were heated to the required temperature and then cooled rapidly *in situ* as described previously [2]. The extent of reaction was determined from DSC measurements on the potassium perchlorate transition and the results are plotted in Fig. 6. They showed that the extent of reaction increased with increasing boron content over the composition range studied, though the amount reacted was low in all cases. These results confirmed observations in the high temperature DSC studies that the magnitude of the pre-ignition exothermic reaction increased with increasing boron content.

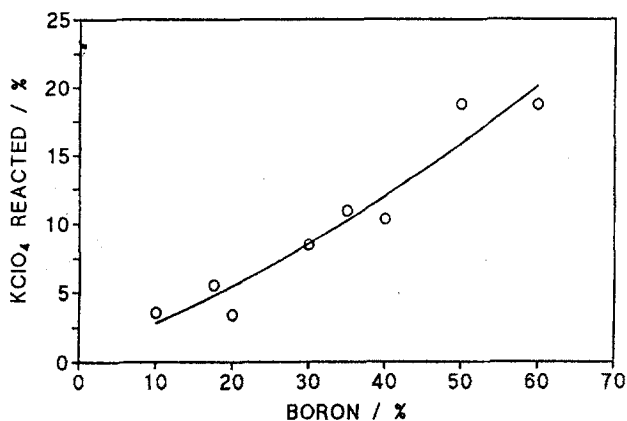


Fig. 6 Plot of amount of KClO_4 reacted against boron content for B- KClO_4 -NC compositions heated to 470°C (measurements by DSC on 5 mg samples heated at 5°C min^{-1} in argon to different temperatures)

Measurements of the extent of reaction as a function of temperature were carried out on the 40%B-59% KClO_4 -1% NC composition by DSC and by chemical analysis for chloride content. The maximum temperature was limited to 500°C to avoid the possibility of an ignition reaction taking place. The percentage of the potassium perchlorate reacted, as determined from the DSC measurements on samples heated to different temperatures, is plotted in Fig. 7. It can be seen that the reaction began in the region of 360°C and that the amount of perchlorate reacted increased in a linear manner with increasing temperature. Only 15% of the per-

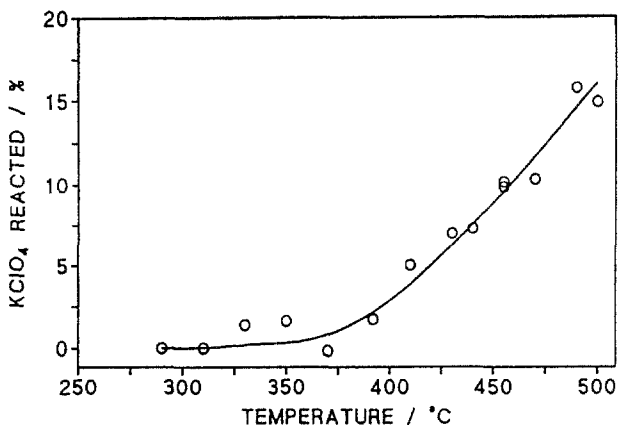


Fig. 7 Plot of % KClO_4 reacted against temperature for a 40% B-59% KClO_4 -1% NC composition (measurements by DSC on 5 mg samples heated at 5°C min^{-1} in argon to different temperatures)

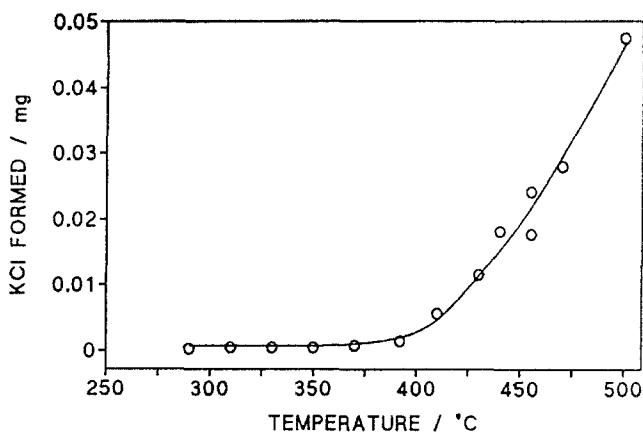
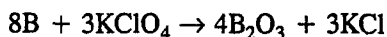


Fig. 8 Plot of weight of KCl formed, per mg of composition, against temperature for the 40% B-59% KClO_4 -1% NC composition (measurements by ISE on 5 mg samples heated at 5°C min^{-1} in argon to different temperatures)

chlorate was found to have reacted on heating to 500°C , whereas for the corresponding zirconium system this level of reaction had been achieved by 420°C .

The measurements of the amount of potassium chloride formed on heating to different temperatures are plotted in Fig. 8. The curve can be seen to be similar in shape to that obtained for the amount of perchlorate reacted. If the chloride measurements are expressed as a percentage of the amount of chloride that would be formed from the total amount of perchlorate present according to the equation:



then a reasonable agreement is given with the values obtained for the percentage perchlorate reacted. The correlation between the perchlorate and chloride measurements provides support for the above equation and indicates that intermediate reactions involving the formation of potassium chlorate do not take place to a significant extent. This was confirmed by a spot test for potassium chlorate on a 40% boron composition heated to 470°C which indicated that below 1% of chlorate was present.

In view of the loss of water observed for the boron itself, it would not be possible to use the mass losses from the above experiments to correct the perchlorate reaction figures for decomposition of perchlorate as had been done for work on the zirconium system [2]. However, thermal analysis-mass spectrometry studies on the 40% boron composition indicated that significant decomposition of perchlorate did not begin until about 500°C. TG studies on potassium perchlorate showed that the addition of B₂O₃, both alone and in the presence of KCl, had much less effect on reducing the temperature of thermal decomposition of potassium perchlorate than did zirconium oxide or nickel oxide.

It appears that the reaction scheme proposed above describes the overall reaction obtained under ignition conditions, since adiabatic combustion calorimetry studies showed that, for compositions containing more than 50% boron, the measured exothermicities were in good agreement with those calculated on the basis of the above equation [9]. The maximum exothermicity was given for compositions in the range 45–50% boron. This is considerably above the stoichiometric value of 17.3% boron, suggesting that only partial reaction of the boron is taking place, even under ignition conditions.

Conclusions

DSC measurements on the boron–potassium perchlorate–nitrocellulose system have shown that the main reaction took place above 500°C, resulting in ignition at about 550°C for compositions containing more than 10% boron. This was in marked contrast to the results obtained for the corresponding zirconium and zirconium/nickel systems, where the exothermic solid state reaction between the metal and the perchlorate took place in the region of 450°C and was considered to be the main component of the pyrotechnic combustion reaction. In the case of the boron compositions, only a low energy pre-ignition reaction was given in this region, which started about 360°C and overlapped with the main reaction exotherm.

Analysis of a range of boron compositions for perchlorate content, after heating to 470°C, showed that the extent of reaction increased with boron content, but was low in all cases. This suggested that the pre-ignition reaction was a surface reaction which was dependent on the amount of boron present. Studies of the extent of reaction in the 40% boron composition as a function of temperature confirmed that the reaction began above 360°C and the amount reacted increased in a linear manner with temperature. Only 15% of the perchlorate was found to have reacted on heating to 500°C, whereas for the corresponding zirconium system this level of reaction had been reached by 420°C.

The reduced reactivity of the boron compositions at lower temperatures was reflected in the higher oxidation temperature of boron in air compared with zirconium

and zirconium/nickel alloy. Comparison of the amount of potassium chloride formed with the amount of perchlorate reacted, showed that a major component of the reaction could be represented by the equation: $8B + 3KClO_4 \rightarrow 4B_2O_3 + 3KCl$, and that potassium chlorate was only formed in very small amounts.

Simultaneous TG-DTA-MS studies showed two events which were not observed in the zirconium and zirconium/nickel systems. Firstly, the loss of trace amounts of chlorine and chlorine dioxide in the region of the pre-ignition exotherm and secondly the evolution of hydrogen chloride during the main exothermic reaction around 550°C. The latter event may be attributed to the presence of water, since the MS studies revealed that boron was able to retain water up to at least 600°C.

References

- 1 B. Berger, E. L. Charsley and S. B. Warrington, *Propellants, Explosives, Pyrotechnics*, 20 (1995) 266.
- 2 B. Berger, E. L. Charsley, J. J. Rooney and S. B. Warrington, *Thermochim. Acta*, 255 (1995) 227.
- 3 B. Berger, E. L. Charsley, J. J. Rooney and S. B. Warrington, *Thermochim. Acta*, 269/270 (1995) 687.
- 4 E. L. Charsley, S. B. Warrington and T. T. Griffiths, 26th ICT Conference, Fraunhofer-Institut für Chemische Technologie, 1995, p. 23-1.
- 5 B. Berger, A. J. Brammer and E. L. Charsley, *Thermochim. Acta*, 269/270 (1995) 639.
- 6 E. L. Charsley, S. B. Warrington, T. T. Griffiths and J. Queay, *Proc. 14th International Pyrotechnic Seminar, RARDE*, 1989, p. 763.
- 7 G. Reinhard, B. Berger and S. Engel, 21st ICT Conference, Fraunhofer-Institut für Chemische Technologie, 1990, p. 93-1.
- 8 B. Berger, E. L. Charsley, J. J. Rooney and S. B. Warrington, 26th ICT Conference, Fraunhofer-Institut für Chemische Technologie, 1995, p. 80-1.
- 9 B. Berger, unpublished work.