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Quantitative studies on the zirconium–potassium perchlorate–nitrocellulose pyrotechnic system using differential scanning calorimetry and chemical analysis

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Abstract

Differential scanning calorimetry and chemical analysis, using ion specific electrodes, have been used to follow quantitatively the solid state reaction in the region of 400°C, between zirconium and potassium perchlorate in the presence of nitrocellulose. Comparison of the amount of potassium chloride formed in the reaction with the amount of perchlorate reacted has shown that the solid state reaction may be represented by the equation $2Zr + KClO_4 \rightarrow 2ZrO_2 + KCl$. DSC has been found to provide an excellent ancillary method for the determination of the amount of potassium perchlorate reacted.

Keywords: DSC; Nitrocellulose; Potassium perchlorate; Pyrotechnics; Zirconium

1. 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 in the region of 400°C,

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which overlapped with the decomposition of unreacted potassium perchlorate [1]. The reaction, which was found to be influenced significantly by the presence of small amounts of nitrocellulose, was considered to take place according to the equation $2Zr + KClO_4 \rightarrow 2ZrO_2 + KCl$. The work discussed in this paper is concerned with quantitative measurements on this solid state reaction by differential scanning calorimetry (DSC) and chemical analysis, using ion-specific electrodes (ISE), to measure potassium perchlorate and chloride contents of the reaction products formed at different temperatures.

It was shown that the aerial oxidation of zirconium started at about 210°C which was well below the temperature at which it reacted with potassium perchlorate [1]. Therefore, to make quantitative measurements on the solid state reaction, it is necessary to reduce the oxidation of the zirconium to a minimum. In addition to its effects on the solid state reaction, it is not possible to distinguish by chemical analysis between the reaction shown above and individual reactions involving the oxidation of zirconium and the decomposition of the perchlorate, i.e. $Zr + O_2 \rightarrow ZrO_2$ and $KClO_4 \rightarrow KCl + 2O_2$. It was necessary, therefore, to establish an experimental procedure to obtain DSC results with minimal oxidation of zirconium and this is discussed in the next section.

Potassium perchlorate gives a well defined solid–solid transition in the region of 300°C and is one of the Certified Reference Materials developed by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) for the temperature calibration of DSC and DTA equipment [2]. The material has been recommended as a potential enthalpy standard [3] and, in a discussion of the compositional analysis of potassium perchlorate–aluminium–barium nitrate mixtures, Hogan et al. [4] have suggested that the area of the solid–solid transition peak could be used as a semi-quantitative estimate of the amount of perchlorate present in a mixture. An estimated accuracy of the method of ±5% was given.

In the present work, it was hoped to use the change in the perchlorate transition peak area to measure the amount of potassium perchlorate reacted when zirconium compositions were heated to different temperatures. This would be carried out by measuring the peak area first obtained on heating to the desired temperature, cooling the sample in the DSC apparatus and reheating to measure the new peak area. Because the sample would not be moved between experiments and the measurements would be made on a relative basis, it was considered that it should be possible to achieve an accurate measure of the extent of reaction, providing no complicating factors were encountered.

2. Experimental

2.1. Materials

The zirconium (Degussa grade CX) had a mean particle size of 1.7 μm, and a purity of 96.5%. The potassium perchlorate had a particle size of less than 60 μm, and a purity of more than 99%. The nitrocellulose was type 220.E, with a nitrogen content of 12.1%. The compositions were prepared in a Turbula mixer before granulation with the nitrocellulose to give a grain size of about 0.5 mm.

2.2. Thermal analysis measurements

Preliminary DSC studies were made using a DTA apparatus, designed for studying pyrotechnic mixtures [5], which had been modified by the incorporation of a chromel heat flux plate. The experiments were carried out in alumina crucibles 6 mm in diameter and 4 mm high with loose-fitting platinum lids. A sample mass of 5 mg and a heating rate of 10°C min^{-1} were used for the majority of the experiments, which were performed in an atmosphere of argon flowing at 400 cm^3 min^{-1}. In order to reduce the aerial oxidation of the zirconium, a small inconel boat containing zirconium was placed inside the DSC head and two further boats containing zirconium were placed on top of the lid of the DSC head.

Quantitative DSC measurements on the solid state reaction in the region 300–500°C were carried out using a Du Pont 9900 DSC system. Samples of 5 mg were heated at 5°C min^{-1} in alumina crucibles 6 mm in diameter and 4 mm high with loose-fitting platinum lids. The experiments were carried out in high purity argon which had been passed through scrubbers to remove oxygen (Chrompak Model 7970) and water. The flow rate through the sample chamber was maintained at 50 cm^3 min^{-1}. To reduce the possibility of back-diffusion of air into the sample chamber, argon was also passed through the coolant port at 200 cm^3 min^{-1}.

In addition, two inconel pans each containing 15 mg zirconium were placed symmetrically on one side of the constantan heat flux plate to act as internal oxygen getters and a third crucible containing zirconium was placed on the silver lid of the sample chamber. Fresh zirconium oxygen getter samples were used in all experiments and by recording their mass changes it was possible to assess the quality of the atmosphere in each individual experiment. Before commencing an experiment, the complete system was slowly evacuated to below 10 Torr using a Leybold Minni vacuum pump attached to the vacuum outlet. Argon was then slowly introduced via the coolant inlet to bring the pressure back to atmospheric. This procedure was carried out four times in all.

Samples for chemical analysis were prepared by cooling the residues when the required temperature had been reached, while maintaining the inert atmospheric conditions. In order to increase the natural cooling rate of the DSC unit, helium, cooled by an ice–salt mixture, was introduced in place of argon through the coolant port using the same flow rate. When the sample temperature reached 250°C, the temperature was held constant and the helium was changed back to argon. The sample was then reheated to 330°C, to measure the peak area of the potassium perchlorate phase change in the reacted material. The sample was finally cooled to below 150°C in argon. Experiments with 5 mg of zirconium in alumina crucibles with platinum lids showed that the level of oxidation on heating to above 500°C was below 1%.

Simultaneous TG-DTA-MS studies were carried out using a Stanton Redcroft STA 1500 TG–DTA unit linked to a VG Gas Analysis Micromass PC 300 amu range quadrupole mass spectrometer, under the conditions described previously [1].

2.3. Measurement of potassium perchlorate and potassium chloride in reaction products using ion specific electrodes

Measurement of the potassium perchlorate and potassium chloride content of reaction products, prepared by heating compositions in the Du Pont DSC apparatus to different temperatures, was carried out using ion specific electrodes. The measurement system was based on an Orion Model 720A pH/concentration meter used in conjunction with a Model 33-81 perchlorate electrode, a Model 94-17B chloride electrode and a Model 90-02 reference junction.

The perchlorate electrode was calibrated using solutions prepared from Analytical Reagent grade potassium perchlorate. Preliminary tests showed that the presence of zirconium and the possible reaction products zirconium oxide (prepared by the oxidation of zirconium), potassium chlorate, potassium chloride and carbon (lamp black) did not influence the measurements. The chloride electrode was calibrated using solutions prepared from a standard 0.100 M solution of sodium chloride supplied by Orion (Code 941706). Potassium perchlorate and the above mentioned possible reaction products were found not to affect the chloride measurements. The calibration of both electrodes was checked several times during a given series of measurements on reaction products.

Solutions were prepared for analysis by transferring the sample crucible and lid to a 100 cm^3 graduated flask. The residue was extracted using cold distilled water and the solution was made up to the mark. 40 cm^3 portions were then filtered using a 0.2 μm Whatman Anatop 25 syringe filter to remove any solid residues. The filtrates were transferred to 100 cm^3 beakers and measured using the appropriate electrode after addition of an ionic strength adjuster.

Spot tests for potassium chlorate were also carried out on the filtrates by the manganese sulphate–phosphoric acid test [6].

3. Results and discussion

3.1. Preliminary DSC measurements on a range of zirconium–potassium perchlorate–nitrocellulose compositions

The previous TG–DTA–MS studies [1] had concentrated on the fuel-lean compositions containing 10% zirconium in order to accentuate any effects due to the addition of nitrocellulose. In order to choose the most suitable composition for the present quantitative studies, a series of experiments was carried out on a range of zirconium–potassium perchlorate–nitrocellulose compositions containing 10–90% zirconium and 1% nitrocellulose. These studies were performed using the DSC unit for ignition studies with the additional aim of determining the conditions required to obtain non-ignition conditions, thereby avoiding possible damage to the instrument by the vigorous ignition reactions which can take place in this pyrotechnic system. Duplicate experiments were carried out on each composition; the first was run over the range ambient to 600°C and the second up to 800°C to observe the fusion peak for any potassium chloride formed in the reaction.

The measurements showed that non-ignition conditions appeared to be achieved in all cases, although for the compositions containing 50% and above of zirconium, the reaction became extremely rapid in the final stages. Typical curves are shown in Fig. 1 and confirm the features observed previously for the 10% zirconium composition [1]. The first reaction was the exothermic decomposition of nitrocellulose at about 200°C which was barely visible on the scale of the diagram and this was followed by the endothermic phase change of potassium perchlorate at 300°C. This transition was followed by the exothermic reaction between zirconium and potassium perchlorate leading to the eutectic melt of $KClO_4$–KCl at about 505°C and the exothermic decomposition of unreacted potassium perchlorate. The latter features decreased significantly as the zirconium content of the compositions was increased. The high temperature endotherm at about 770°C was due to the fusion of potassium chloride.

Comparision of the peak sizes for the main exothermic reaction indicated a rapid increase in the exothermicity of reaction up to the 40% zirconium level. Above this level it was difficult to make an estimate of the reaction exothermicity due to the very rapid reaction in the final stages. It would appear, however, that the exothermicity only became significantly reduced above the 70% zirconium level.

A quantitative study using the Du Pont 9900 DSC to measure the apparent reaction exothermicity as a function of the zirconium content of the composition is now in progress [7].

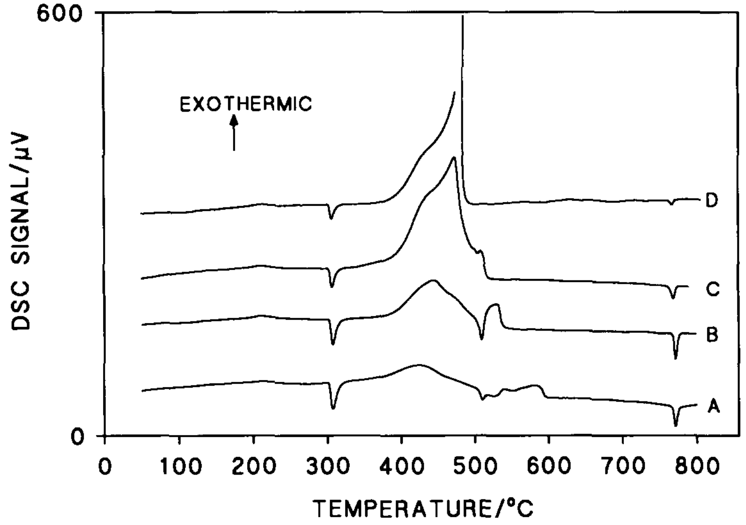

Fig. 1. DSC curves for (A) 10%Zr–89%$KClO_4$–1%NC, (B) 20%Zr–79%$KClO_4$–1%NC, (C) 40%Zr–59%$KClO_4$–1%NC and (D) 60%Zr–39%$KClO_4$–1%NC compositions (sample mass, 5 mg; heating rate, 10°C min^{-1}; atmosphere, argon).

Table 1
DSC peak area and extrapolated onset temperature (EOT) measurements on the solid–solid phase transition of potassium perchlorate

Sample	Peak area/(J g^{-1})		Diff./%	EOT/°C		Diff./°C
	1st Heat	2nd Heat		1st Heat	2nd Heat	
1	109.6	108.6	−0.9	302.0	301.7	−0.3
2	112.0	111.4	−0.6	302.0	301.5	−0.5
3	108.9	107.5	−1.3	302.2	301.9	−0.3
4	110.5	110.3	−0.2	302.1	301.8	−0.3
5	108.6	108.5	−0.1	302.2	302.0	−0.2

3.2. Preliminary DSC studies on the measurement of the phase transition of potassium perchlorate

A series of measurements was carried out using the Du Pont 9900 DSC unit to investigate the reproducibility of area measurements for the potassium perchlorate phase transition with respect to the first and second heating. The results are given in Table 1 and show that there was excellent agreement between the two sets of data and hence provided the basis for the determination of the amount of perchlorate reacted. The extrapolated onset temperatures for the transitions are also listed in Table 1 and it can be seen that both the temperature and peak area measurements show good reproducibility. It would appear, therefore, that this material should be considered further as part of the ICTAC Standardisation Committee's programme for the development of accurate temperature and enthalpy calibrants for DSC and DTA [8]. Although the peak area measurements showed no significant difference between the first and second heating experiments, the extrapolated temperatures showed a small decrease.

3.3. Measurement of the extent of reaction in the 40% zirconium–59% potassium perchlorate–1% nitrocellulose composition as a function of temperature

Following the preliminary high temperature DSC experiments, the 40%Zr–59%$KClO_4$–1%NC composition was chosen for detailed investigation using the Du Pont 9900 system, because it gave a high level of exothermicity and compositions containing higher levels of zirconium gave the very fast reaction at higher temperatures, which was difficult to measure quantitatively. A typical DSC curve for the 40% zirconium composition is shown in Fig. 2 and closely resembled that obtained using the DSC unit designed for ignition studies.

The percentage of the potassium perchlorate reacted, as determined from the ISE measurements on samples heated on different temperatures, is plotted in Fig. 3. The values can be seen to lie on a well defined curve and provide a quantitative measure of the extent of reaction as a function of temperature. The reaction could be seen to start in the region of 350°C, became rapid above 400°C and was completed by 510°C.

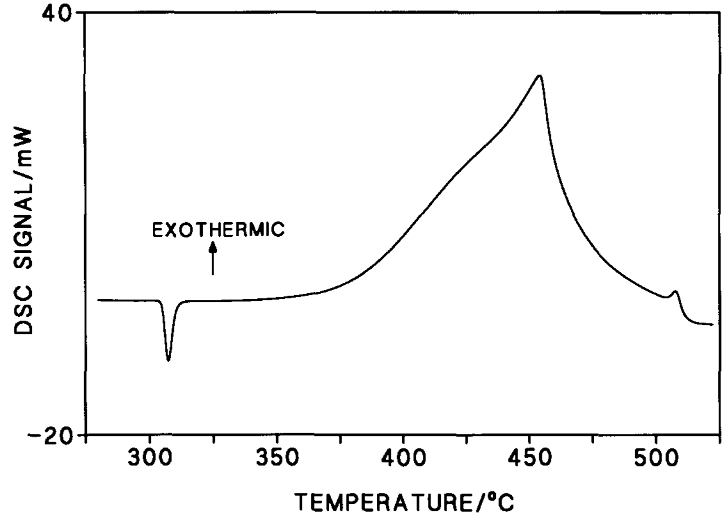

Fig. 2. DSC curve for a 40%Zr–59%$KClO_4$–1%NC composition (sample mass, 5 mg; heating rate, 5°C min^{-1}; atmosphere, argon).

DSC measurements on the residues showed well defined peaks for the solid–solid transition of unreacted perchlorate, although the single transition observed for the perchlorate alone showed evidence of a double peak in the reaction products and this is illustrated in Fig. 4. The measurements on the amount of perchlorate reacted

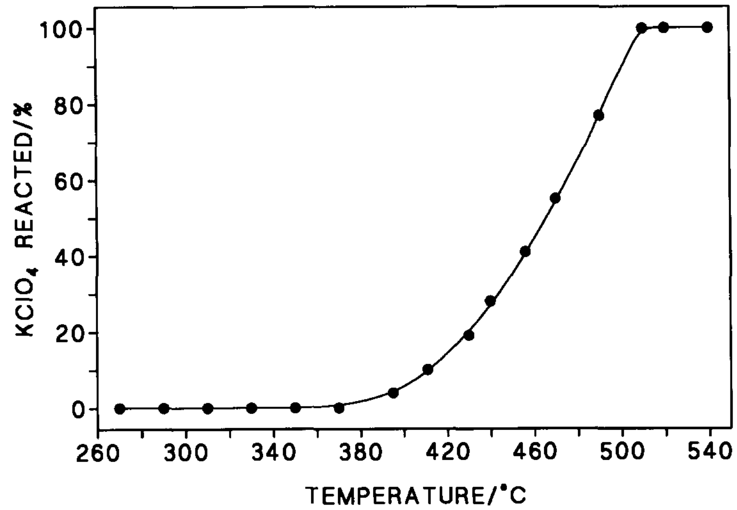

Fig. 3. Plot of percentage $KClO_4$ reacted against temperature for a 40%Zr–59%$KClO_4$–1%NC composition (measurements by ISE on 5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

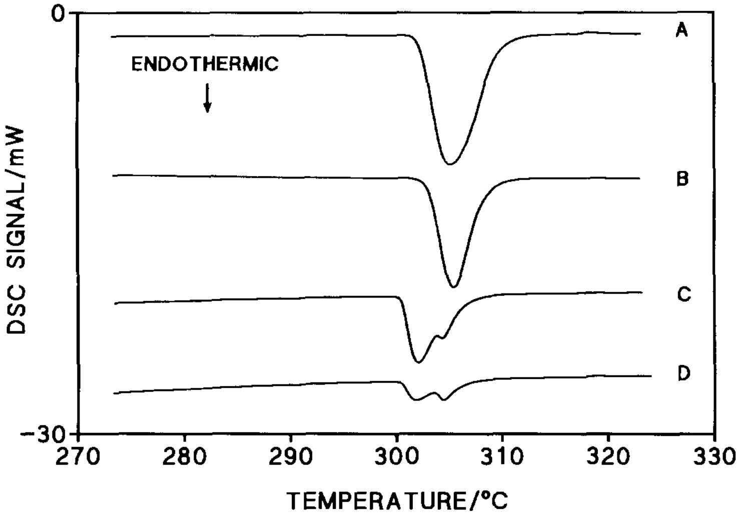

Fig. 4. DSC curves showing the solid–solid transition in potassium perchlorate: (A) for $KClO_4$ and for a 40%Zr–59%$KClO_4$–1%NC composition, (B) unheated, (C) heated to 440°C, and (D) heated to 490°C (sample mass, 5 mg; heating rate, 5°C min^{-1}; atmosphere, argon).

by DSC were in excellent agreement with those measured by ISE and this correlation is shown in Fig. 5. In the majority of cases the agreement between the measurements was better than 2% and the DSC technique clearly provides a useful method for the determination of perchlorate content of pyrotechnic reaction

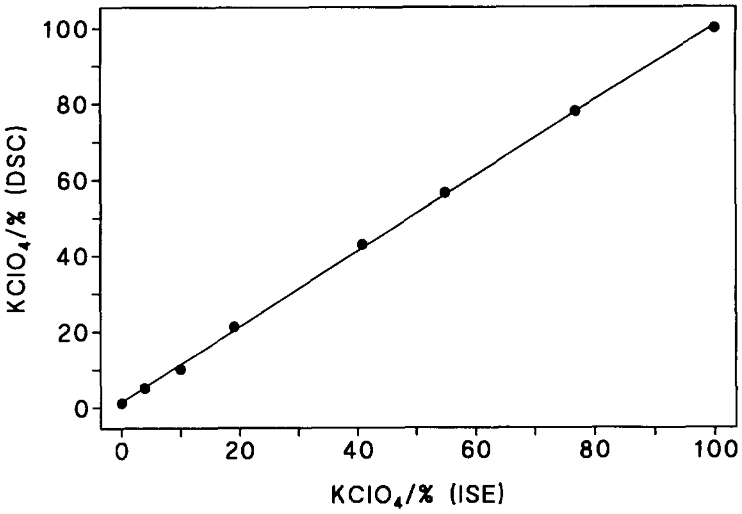

Fig. 5. Plot of percentage $KClO_4$ reacted measured by DSC against percentage $KClO_4$ reacted measured by ISE for the 40%Zr–59%$KClO_4$–1%NC composition (5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

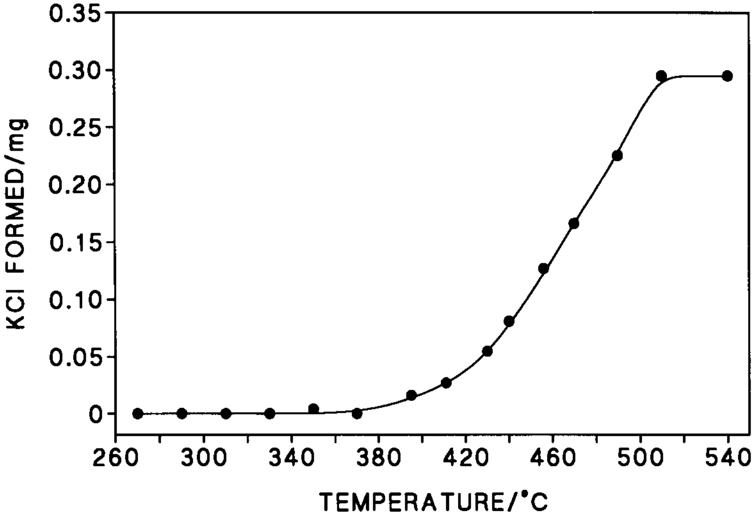

Fig. 6. Plot of mass of KCl formed per mg of composition, against temperature for the 40%Zr-59%$KClO_4$-1%NC composition (5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

products. The distortion of the transition peak as the extent of reaction increases has not affected the area measurements.

The results of the measurements on the amount of potassium chloride formed in the reaction at different temperatures are plotted in Fig. 6. The curve can be seen to be very similar in shape to that obtained for the amount of perchlorate reacted as a function of temperature. To test the validity of the reaction equation postulated previously, the chloride values have been expressed as a percentage of the amount of chloride that would be formed from the total amount of perchlorate present according to the equation $2Zr + KClO_4 \rightarrow 2ZrO_2 + KCl$.

The calculated values for the percentage potassium chloride formed have been plotted against the percentage potassium perchlorate reacted in Fig. 7. The excellent correlation between the perchlorate and chloride measurements lends quantitative support to the postulated reaction equation and suggests that an intermediate reaction involving the formation of potassium chlorate, which had been observed at low levels in the decomposition of potassium perchlorate [9], did not take place to a significant extent in the presence of zirconium. This observation was supported by X-ray diffraction measurements on the residues formed at different temperatures which showed ZrO_2 and KCl to be the only reaction products. The absence of potassium chlorate in the reaction products was also confirmed by negative spot tests carried out on the filtrates prepared from the residues of the heating experiments.

The extent of reaction has also been followed as a function of temperature by cumulative area measurements on the DSC peaks. The partial areas were measured at the temperatures of the individual heating experiments. The cumulative DSC

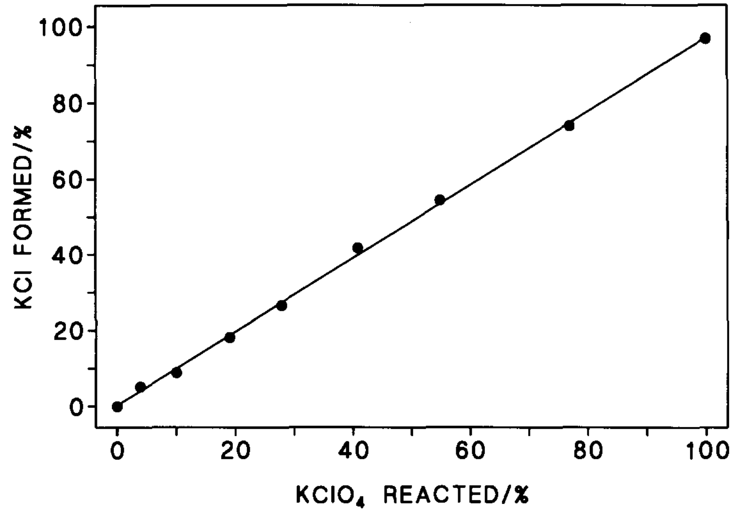

Fig. 7. Plot of percentage KCl formed against percentage $KClO_4$ reacted for the 40%Zr–59%$KClO_4$–1%NC composition (5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

areas have been plotted against the corresponding amount of potassium perchlorate reacted and this is shown in Fig. 8. It can be seen from the figure that there is a linear correlation between the two sets of measurements up to the level at which 40% of the potassium perchlorate has reacted. Above this reaction level the residues started to show a loss in mass indicating decomposition of the perchlorate.

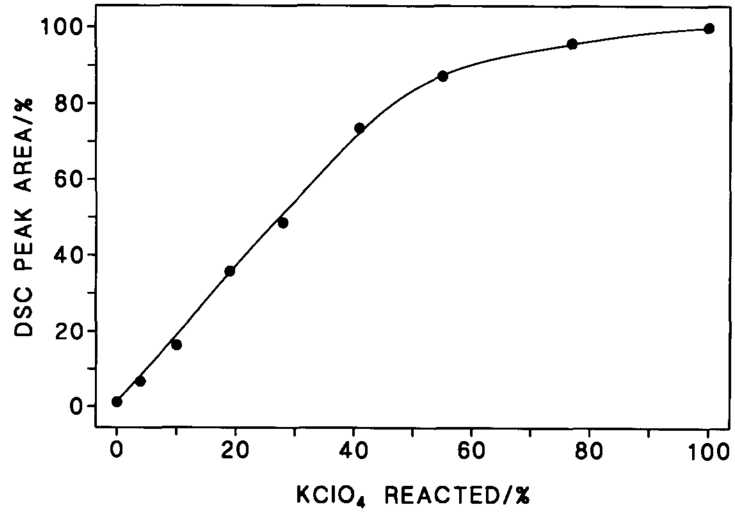

Fig. 8. Plot of percentage DSC peak area against percentage $KClO_4$ reacted for the 40%Zr–59%$KClO_4$–1%NC composition (sample mass, 5 mg; heating rate, 5°C min^{-1}; atmosphere, argon).

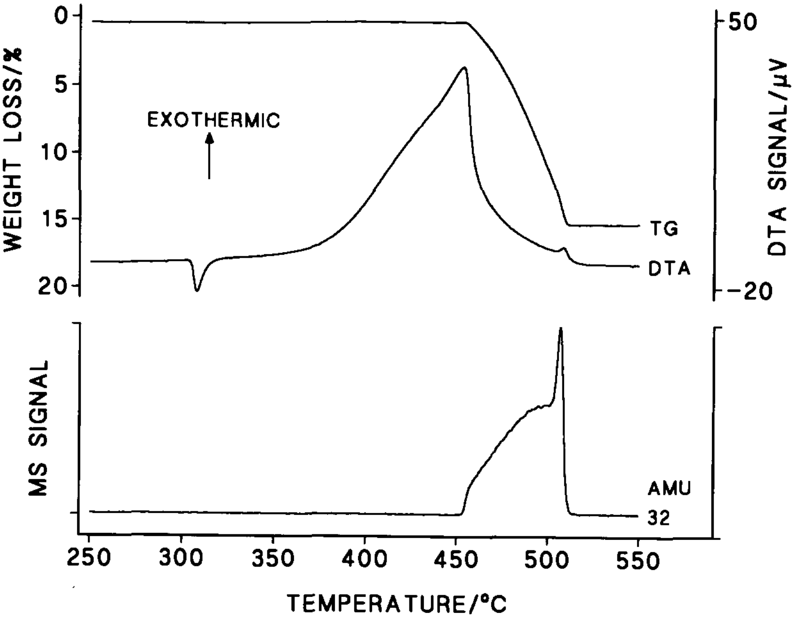

Fig. 9. TG–DTA–MS curves for a 40%Zr–59%$KClO_4$–1%NC composition (sample mass, 10 mg; heating rate, 5°C min^{-1}; atmosphere, argon).

Simultaneous TG–DTA–MS studies on the 10%Zr–89%$KClO_4$–1%NC composition showed that the sample began to lose mass in the region of the DTA peak maximum due to the decomposition of potassium perchlorate which was catalysed by the presence of the reaction products KCl and ZrO_2. It can be seen from the simultaneous TG–DTA–MS plot for the 40% zirconium composition in Fig. 9 that decomposition of the perchlorate began in the region of the DTA peak maximum at about 455°C. The rate of oxygen evolution showed a sharp increase in the final stages of reaction, accompanied by a small exothermic peak. This is attributed to the acceleration of the decomposition of the small amount of perchlorate remaining by the formation of the $KClO_4$–KCl eutectic melt in the region of 505°C.

Because the onset of the perchlorate decomposition reaction overlapped with the solid state reaction, the perchlorate measurements at high temperatures do not provide a direct indication of the extent of the solid–solid reaction. The results have therefore been corrected by calculating the extent of the perchlorate decomposition from the measured mass losses of the residues using the equation $KClO_4 \rightarrow KCl + 2O_2$. The amount of perchlorate decomposed has then been subtracted from the overall amount of perchlorate reacted to enable an approximate estimate of the extent of the solid state reaction to be made. This is illustrated in Fig. 10. It would appear from these measurements that the solid state reaction is completed in the region of 460°C and that there is not a great deal of overlap with the perchlorate decomposition.

From these results it would appear that about 40% of the potassium perchlorate present reacted with the zirconium in the solid state reaction. This gives a figure of 23% perchlorate by mass of the composition. This compares with a value of 30.4% calculated from the proposed reaction equation, or 25.8% if the value of 85% purity derived from TG oxidation studies [1] is assumed for the zirconium. Use of the latter figure indicated that the solid state reaction has gone to approximately 90% completion.

4. Conclusions

It has been shown that by careful attention to the experimental procedure it is possible to make quantitative studies on the solid state reaction between zirconium and potassium perchlorate in the presence of nitrocellulose. The perchlorate analysis by ISE has enabled the amount of potassium perchlorate reacted to be established quantitatively as a function of temperature.

By comparison of the DSC peak area measurements on the potassium perchlorate transition before and after reaction with those from the perchlorate electrode, the DSC technique has been found to provide an excellent ancillary method for the determination of the extent of the perchlorate reaction. In addition a direct correlation was observed between the exothermicity of reaction by DSC and the amount of potassium perchlorate consumed for reaction in the temperature region below the onset of the decomposition of perchlorate.

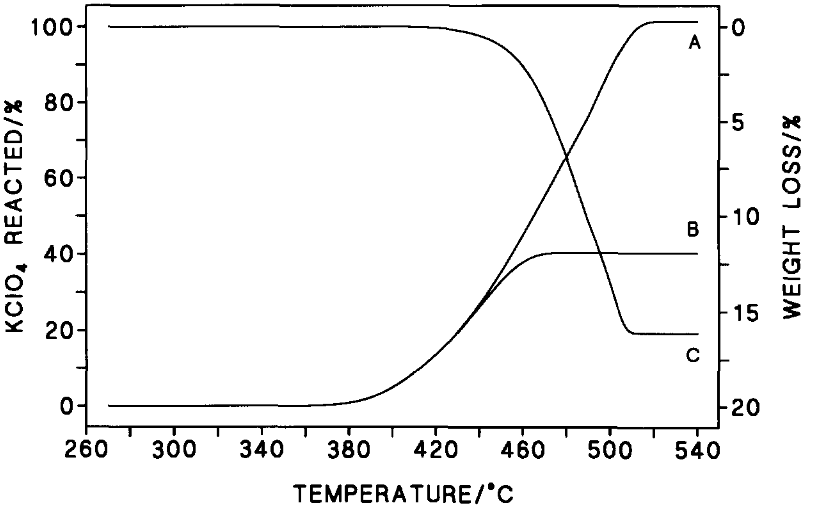

Fig. 10. Plot of percentage $KClO_4$ reacted (A) total, (B) by solid state reaction; and (C) mass loss against temperature for the 40%Zr–59%$KClO_4$–1%NC composition (5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

Comparison of the amount of potassium chloride formed in the reaction with the amount of perchlorate reacted has shown that the solid state reaction may be represented by the equation $2Zr + KClO_4 \rightarrow 2ZrO_2 + KCl$ and that potassium chlorate, which has been found as an intermediate in the decomposition of potassium perchlorate, is not formed in significant quantities in the presence of zirconium.

The mass losses measured for the samples heated to different temperatures have enabled the extent of the solid state reaction to be estimated in the region where the potassium perchlorate was decomposing and indicated that the reaction had gone to approximately 90% completion.

The approach described in this paper, of DSC measurements combined with ISE measurements, has also been used to quantify the influence of nitrocellulose on the reaction between zirconium and potassium perchlorate [7].

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