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Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part 1. Thermal analysis

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Abstract

Thermal analysis has been used to examine the processes occurring during controlled heating of the four binary pyrotechnic systems Mn/BaO_2, Mn/SrO_2, Mo/BaO_2 and Mo/SrO_2. The main exothermic events are observed to correspond approximately with the onset of oxidant decomposition. A pre-ignition reaction is tentatively identified in the Mn/BaO_2 system. Oxidation of the metal fuels is generally incomplete, probably because of the formation of protective layers of product.

Ternary systems containing either mixed fuels or mixed oxidants have also been studied. No interactions between the fuels or between the oxidants is observed.

X-Ray powder diffraction, infrared spectroscopy and scanning electron microscopy have been used to examine products and intermediates.

INTRODUCTION

Barium and strontium peroxides were selected as oxidants in a fundamental physicochemical study of binary pyrotechnic systems on account of their apparently simple decomposition stoichiometry. The choice of fuel was then governed by the requirements of a self-sustaining reaction at combustion temperatures below the melting point of the platinum/rhodium thermocouples (≈1760°C) used for recording temperature–time profiles during burning, and at burning rates not exceeding the response of the sensors used to monitor combustion. Both manganese and molybdenum metal powders satisfied the above requirements.

The use of BaO_2 and SrO_2 as oxidants in pyrotechnic mixtures is widespread, but relatively little has been published in the open chemical literature. BaO_2 has been used mainly in delay systems [1, 2] and SrO_2 in tracer compositions [3–6].

Amongst the several pyrotechnic systems reported in the significant

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early studies by Spice and Staveley [7, 8] and Hill et al. [9, 10] were those of Fe/BaO_2, Mn/BaO_2, Mo/BaO_2 and S/BaO_2.

Hogan and Gordon [11] used thermogravimetry (TG) and differential thermal analysis (DTA) to investigate the ternary system of Mg/BaO_2/calcium resinate. As part of their study they also considered the binary system of Mg/BaO_2 and proposed the stoichiometry

$$\mathrm{Mg(s) + BaO_2(s) \rightarrow BaO(s) + MgO(s)}$$

with an ignition temperature of 540°C and an activation energy of ignition of 155 kJ mol^{-1}. The value for the activation energy was obtained from an Arrhenius plot using the reciprocals of times to ignition at various isothermal temperatures as measures of the rate coefficients.

DTA studies of the Mg/BaO_2/acaroid ternary system [12] showed that a binder–oxidant reaction was responsible for lowering the ignition temperature of the Mg/BaO_2 binary system from above 500 to about 350°C.

Nakahara and Hikita [13] measured significant gas pressures during the combustion of the Mo/BaO_2 system.

The Se/BaO_2 system is a commonly used delay mixture in the USA [14] and has been investigated by Johnson [2]. He distinguished three processes occurring at different temperatures, of which two were below the ignition temperature. The first process led to an increase in contact area between the selenium and the BaO_2 by the migration of the selenium atoms which formed a surface coating on the BaO_2 at temperatures below the ignition point. It was not established whether this migration of selenium atoms occurred in the solid state or in the vapour phase. The second process was an exothermic reaction between selenium and BaO_2 which was not self-sustaining. The third process was the self-propagating concurrent reaction described by the equations

$$\mathrm{Se(s) + 3BaO_2(s) \rightarrow BaSeO_4(s) + 2BaO(s)} \qquad \Delta H = -400\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{2Se(s) + 2BaO_2(s) \rightarrow BaSeO_4(s) + BaSe(s)} \qquad \Delta H = -508\ \mathrm{kJ\ mol^{-1}}$$

Recently, Yoshinaga et al. [15] investigated the reactions between molybdenum and BaO_2 using TG, DTA, X-ray powder diffraction and chemical analysis. They observed the thermal decomposition of BaO_2 at a temperature of about 400°C and identified small amounts of $BaCO_3$ and $Ba(OH)_2$ in the BaO_2 as a result of exposure to the air or due to grinding. The reaction between molybdenum and BaO_2 occurred at 385°C and was retarded by the presence of $BaCO_3$. The heat of the combustion reaction increased as the amount of molybdenum was increased. They quoted values for the ignition temperature ranging from 425 to 500°C and for the ignition energy of from 11 to 12 kJ mol^{-1}.

Decomposition of peroxides

Many studies of the decompositions of peroxides have been reported [16–24]. Decomposition to the solid oxide and gaseous oxygen is generally agreed to be endothermic and reversible. The values reported for the decomposition temperature of BaO_2 vary with the partial pressure of oxygen and with the sample mass, from about 840°C for gram samples in 1 atm of O_2, to 670°C for milligram samples in air. Values reported for the enthalpy of dissociation of BaO_2 are 80.0 kJ mol^{-1} [16], 80.8 kJ mol^{-1} [17] and 74.5 kJ mol^{-1} [18].

Hogan and Gordon's investigation [11] of the decomposition of BaO_2, using TG and DTA, revealed that a mass loss, equivalent to the loss of one atom of oxygen per BaO_2 unit, began at about 600°C, but was not accompanied by a thermal event in their DTA trace. DTA traces of Mg/BaO_2 reported by Barton et al. [12] showed no exothermic event at temperatures around 300°C. Beck [25], using simultaneous TG/DTA, reported a mass loss beginning at about 650°C for the decomposition of BaO_2, which accelerated to a maximum at 800°C. His DTA trace showed an endothermic event beginning at approximately 800°C.

The decomposition of SrO_2 has been proposed [19, 20] to be a two-step process

$$SrO_2(s) \rightarrow SrO(s) + O(ads)$$

$$O(ads) + SrO_2(s) \rightarrow SrO(s) + O_2(g)$$

A possible explanation for this behaviour was the formation of a layer of a solid solution of oxygen in SrO_2. As this layer begins to form it temporarily stops the dissociation, and dissociation in this hindering layer only becomes measurable at higher temperatures.

In later work Azuma et al. [24] did not support a two-step mechanism. They also reported that the decomposition of most peroxides accelerates under atmospheres of H_2O or CO_2, where the peroxides form hydroxides and carbonates, respectively.

The reported temperatures of decomposition of SrO_2, under different experimental conditions, range from 212 to 410°C. The enthalpy of dissociation of SrO_2 has been reported as 56.5 kJ mol^{-1} [22], 41.8 kJ mol^{-1} [20] and 48.0 kJ mol^{-1} [17].

Both the temperature and the energy requirements for dissociation are lower for SrO_2 than for BaO_2. This agrees with the sequence of decreasing stability of the alkaline earth peroxides shown by Vannerberg [26] to be $Ba > Sr > Ca$, with dissociation pressures (atm) at 100°C of 10^{-13}, 0.1 and 50 respectively.

EXPERIMENTAL

Materials

The materials used were (A) oxidants: BaO_2 (Merck) 86.0 ± 0.1% pure, median particle diameter 36.6 μm, density 4.96 g cm^{-3}; SrO_2 (Bernardy) 88.0 ± 0.1% pure, median particle diameter 3.5 μm, density 4.56 g cm^{-3}; (B) fuels: Mn powder (Cerac) 99.95% pure, median particle diameter 16.6 μm, density 7.20 g cm^3; Mo powder (Cerac) 99.9% pure, median particle diameter 34.4 μm, density 10.20 g cm^{-3}.

The compositions of the binary pyrotechnic mixtures are stated as percentages, by mass, of the fuel. The compositions of the ternary systems are quoted as percentages by mass of each constituent. The constituents of all the pyrotechnic mixtures were mixed by end-over-end tumbling or by brushing through an appropriately sized sieve.

The unreacted starting materials and the products of reaction during thermal analysis and ignition studies were characterized using X-ray powder diffraction (XRD) and infrared (IR) spectroscopy. Scanning electron microscopy (SEM) was also used to detect the changes in external appearance during ignition and controlled heating experiments.

Apparatus

A Perkin Elmer DSC-7 differential scanning calorimeter and TGA-7 thermogravimetric analyser coupled to an IBM compatible microcomputer were used. Samples (<20 mg) were heated in platinum pans and the carrier gas was either N_2 or O_2.

RESULTS AND DISCUSSION

Thermal analysis of the oxidants

Barium peroxide

Both thermal analysis and burning experiments (Part 2 of this series, ref. 27), indicated different behaviour for BaO_2 samples from different sources. A DSC trace for Merck BaO_2 heated in N_2 at 10°C min^{-1} is shown in Fig. 1. The two low temperature endotherms (<110°C) were caused by the loss of loosely adsorbed water and showed great variability from sample to sample. These endotherms appeared unchanged in the DSC traces of pyrotechnic mixtures containing BaO_2 (see below). The DSC traces did not indicate any melting.

A reproducible endotherm with onset temperature of about 360°C, not reported in other thermal analyses of BaO_2 [11, 12, 16, 25], was not accompanied by a mass change in the corresponding TG trace (Fig. 1). The onset temperature corresponds closely to the onset temperature

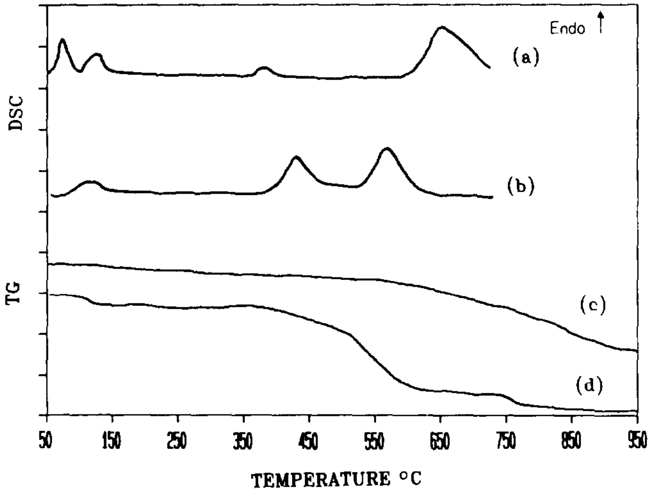

Fig. 1. Thermal analysis of the oxidants in N_2 at 10°C min^{-1}. Curve a, BaO_2 DSC; curve b, SrO_2 DSC; curve c, BaO_2 TG; curve d, SrO_2 TG.

(≈370°C) of a sharp endotherm in the DSC trace for $Ba(OH)_2$. The presence of $Ba(OH)_2$ in samples of BaO_2 has been reported [1, 15, 26] and was shown by XRD and IR to be present in the Merck sample. This endotherm was thus assigned to a complex process in the dehydroxylation of $Ba(OH)_2$ which preceded a mass loss (without enthalpy change) at a higher temperature in the corresponding TG trace of $Ba(OH)_2$. Vannerberg [26] has described the reaction of solid peroxides with gaseous CO_2 to give solid carbonate and $O_2(g)$ and Beyens and Dubois [1] have reported the formation of a surface layer of $BaCO_3$ during the exposure of BaO_2 to a moist atmosphere. The effects of these impurities on the reactions of BaO_2 have been reported [1, 15].

The high temperature (≈600°C) endotherm in the DSC traces for BaO_2 was attributed to decomposition. The expected enthalpy change for the decomposition of BaO_2 to solid BaO and gaseous O_2, calculated from standard enthalpies of formation [28], is 334 J g^{-1}. The measured value was 382 ± 35 J g^{-1} for 86% pure BaO_2 which converts to approximately 450 J g^{-1} for pure BaO_2. This is in good agreement with the value of 473 ± 12 J g^{-1} reported by Till [16]. In O_2 the decomposition endotherm was absent up to the instrument limit of 725°C.

The TG trace for BaO_2 heated in N_2 at 20°C min^{-1} showed a gradual mass loss of 0.71 ± 0.02% of the original mass extending from about 50° up to about 570°C corresponding to the loss of adsorbed water. Decomposition began at about 570°C where the mass loss accelerated up to about 820°C followed by a further acceleration. The mass loss between about 570° and about 820°C was 3.9 ± 0.2% and from approximately 820°C onwards it was 2.5 ± 0.2%. The overall mass loss was thus 7.7 ± 0.2% of the original sample mass. The expected mass loss for the decomposition of pure BaO_2 to solid BaO and gaseous O_2 is 9.5%, which converts to 8.2% for 86% pure BaO_2. There were indications of onset of a further incomplete stage at high temperature ($\approx$900°C), which could be due to the decomposition of $BaCO_3$ impurity. The TG trace in O_2 was similar.

The decomposition of BaO_2 was confirmed [17] to be reversible when the solid residues from the initial DSC scans of BaO_2 were exposed to air for 15 min.

Strontium peroxide

The DSC trace for SrO_2 heated in N_2 at 10°C min^{-1} showed three endotherms (Fig. 1). The low temperature endotherm with onset at approximately 80°C was due to the loss of adsorbed water. The next two endotherms with onset temperatures of about 390 and about 535°C would correspond to the decomposition stages. The estimated enthalpy changes were 185 ± 20 J g^{-1} and 182 ± 29 J g^{-1}, respectively. The expected enthalpy change for the decomposition of SrO_2 to solid SrO and gaseous O_2 is 427 J g^{-1} [30]. The relative sizes of the two endotherms tend to change with heating rate. The total ΔH value for the two endotherms of SrO_2 was 367 J g^{-1} and the value recorded by Fahim and Ford [17] was 402 J g^{-1}.

No intermediate compound was identified. XRD analysis showed that samples heated to about 520°C and cooled for 30 min in N_2 contained little peroxide and consisted mainly of SrO.

In O_2, the onset temperatures of both stages of the thermal decomposition of SrO_2 were increased but were still within the limits of the DSC.

The TG trace for SrO_2 (Fig. 1) heated at 20°C min^{-1} in N_2, confirmed the low temperature loss of adsorbed water with a mass loss of 0.5 ± 0.1% starting at about 100°C. The next mass loss of 13.9 ± 0.1% of the original mass, begins at approximately 385°C with a sharp acceleration at about 500°C. The DTG trace supports the two-step decomposition suggested by the DSC traces. The calculated mass loss for the decomposition of pure SrO_2 to SrO(s) and $0.5O_2$(g) is 13.4% which decreases to 11.8% based on 88% pure SrO_2. The TG traces show a further mass at high temperature probably caused by the decomposition of $SrCO_3$.

If the SrO_2 residues were exposed to the air for about 12 h, some regeneration of peroxide took place. This was demonstrated by the presence of an endotherm at about 400°C in a repeat DSC scan. SrO_2 is thus far less susceptible to regeneration than BaO_2, under these conditions.

Thermal analysis of the fuels

DSC traces of manganese powder heated in N_2 at 20°C min^{-1} showed a reproducible and reversible endotherm at about 675°C with an enthalpy

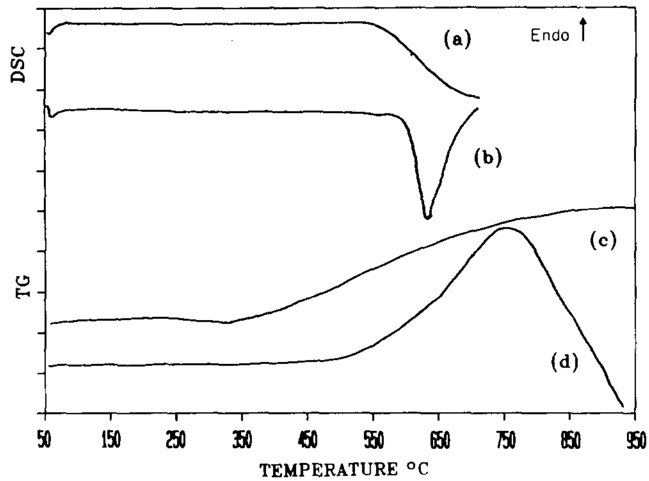

Fig. 2. Thermal analysis of the fuels in O_2 at 20°C min^{-1}. Curve a, Mn DSC; curve b, Mo DSC; curve c, Mn TG; curve d, Mo TG.

change of 14 ± 1 J g^{-1}. This endotherm was assigned to the α–β phase transition which is reported [28] to occur at 700 ± 3°C ($\Delta H = 41$ J g^{-1}). Small and variable exotherms at about 330° and about 450°C were attributed to the oxidation of the manganese powder by small amounts of oxygen and/or water vapour in the instrument.

The DSC trace for manganese powder in O_2 (Fig. 2) showed that oxidation started above 560°C but was incomplete in the temperature range of the DSC. The mass gain that begins above 360°C in the TG curve (Fig. 2) was irreproducible, varying from low values (incomplete oxidation) to 30% (corresponding approximately to formation of MnO(s)). The measured enthalpy for this incomplete exotherm was −0.2 kJ g^{-1} compared to the expected [28] value of −7 kJ g^{-1}.

Molybdenum powder showed no DSC response when heated in N_2 at 20°C min^{-1} in the temperature range of the DSC.

The oxidation of molybdenum powder (Fig. 2) started at about 600°C in the DSC and had an enthalpy change of −4 ± 1 kJ g^{-1}. The expected [28] enthalpy change for formation of MoO_3 is −7.9 kJ g^{-1}. The mass gain above 440°C was about 44% of the original mass which is close to the mass gain expected (50.0%) for the formation of MoO_3. The mass loss at about 750°C was probably caused by the sublimation of the newly formed MoO_3(s). The reported [29] sublimation temperature is 1155°C at 760 mmHg.

Thermal analysis of the binary pyrotechnic systems

Mn/BaO_2 system

Compositions containing from 15 to 65% manganese sustained combustion [27]. The DSC trace for 40% Mn/BaO_2 (≈20 mg) heated in N_2 at

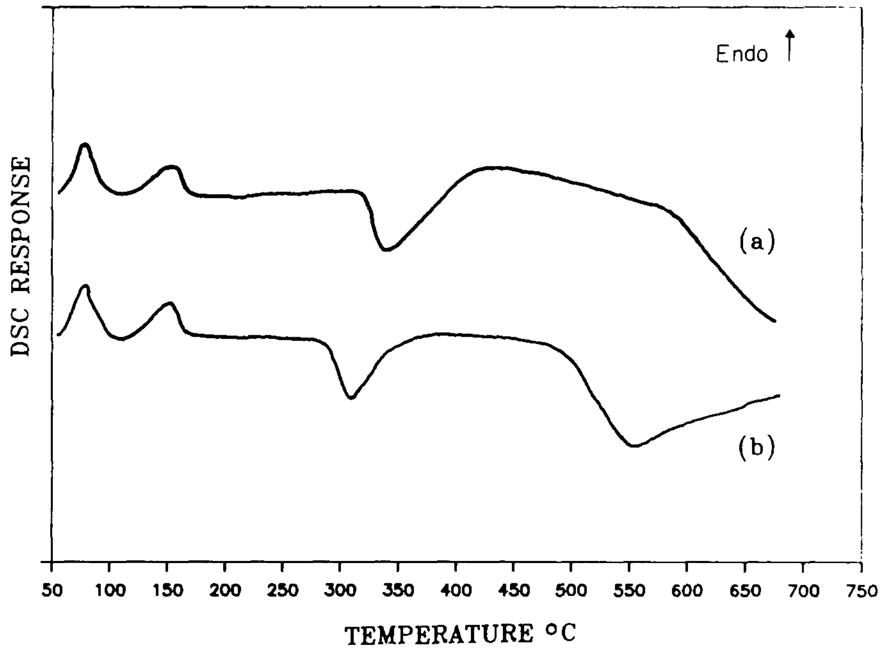

Fig. 3. DSC traces for 40% Mn/BaO_2 heated at 20°C min^{-1}. Curve a, in N_2; curve b, in O_2.

20°C min^{-1} is shown in Fig. 3. The low temperature endotherms due to the loss of adsorbed water from BaO_2 (see above) are followed by two exotherms with onset at about 365°C and about 605°C, respectively. These onset temperatures correspond closely to the onset temperatures of endotherms in the DSC trace for BaO_2 heated alone in N_2 (Fig. 1). The lower temperature exotherm (≈365°C) corresponds closely to the endotherm assigned to the thermal rearrangement of $Ba(OH)_2$ (≈360°C), while the other exotherm (≈605°C) occurs at similar temperatures to the decomposition temperature of BaO_2. The associated enthalpy changes are -76 ± 12 and -142 ± 40 J g^{-1} (incomplete at 725°C), respectively.

Changing the composition (20, 30 and 50% Mn) of the Mn/BaO_2 system affected the DSC trace as shown in Fig. 4. The onset temperature of the large exotherm assigned to the oxidation of manganese, decreased from about 620°C for the 20% composition to approximately 550°C for the 50% composition.

In O_2, the two exotherms had lower onset temperatures than in N_2. The first exotherm (≈350°C) had an onset temperature well below the temperature (≈560°C) at which the manganese was oxidized by the O_2 (Fig. 2) and its enthalpy change was similar to that of the corresponding exotherm (≈365°C) measured when the sample was heated in N_2 (Fig. 3). Thus it appears that similar reactions take place between manganese and

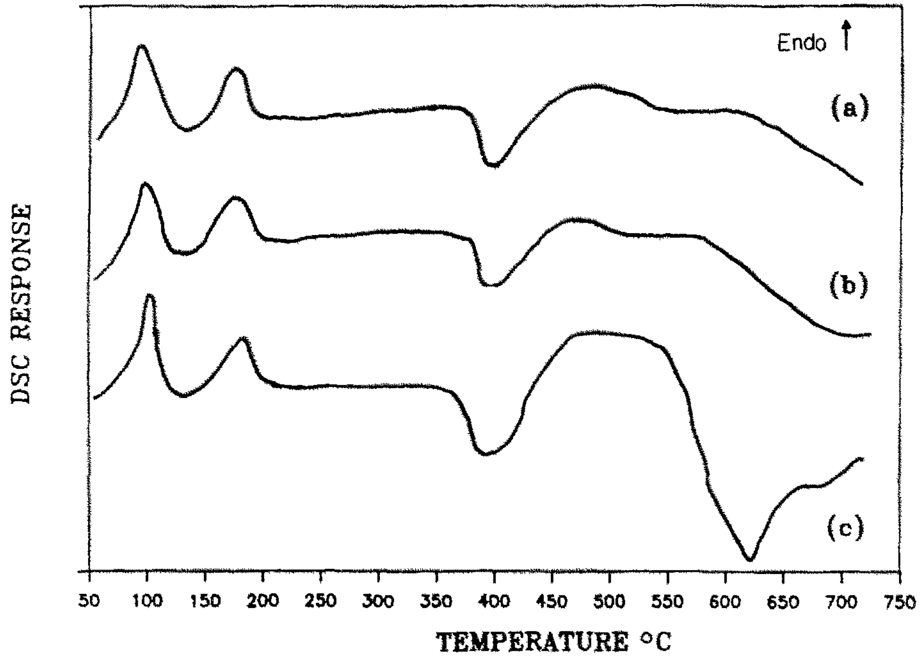

Fig. 4. DSC traces for different compositions of Mn/BaO_2 heated at 20°C min^{-1} in N_2. Curve a, 20% Mn; curve b, 30% Mn; curve c, 50% Mn.

BaO_2 under both inert and oxidizing conditions, except that in O_2 the reactions occur at lower temperatures.

The second exotherm (onset ≈500°C) occurred at temperatures below the onset temperature (≈560°C) of the oxidation of manganese powder by the O_2 carrier gas. The exotherm was incomplete in the temperature range of the DSC and the enthalpy change was smaller than that measured in N_2. If this exotherm was due to the complete oxidation of the manganese by the oxygen gas then, based on the ΔH value for manganese heated alone in O_2, the ΔH value would be expected to be about -80 J g^{-1} of pyrotechnic mixture which is larger than the mean recorded value of about -54 J g^{-1}. This exotherm could thus be due to further oxidation of the products formed at approximately 350°C.

A DSC trace for 40% Mn/$BaCO_3$ heated in N_2 at 40°C min^{-1} from 50 to 725°C showed only the endotherm (≈620°C, $\Delta H = 15 \pm 2$ J g^{-1}) assigned to an allotropic change in manganese.

The DSC trace for 40% Mn/$Ba(OH)_2$ heated at 20°C min^{-1} in N_2 showed endotherms with onset temperatures of about 110°C for the loss of adsorbed water from $Ba(OH)_2$, and about 265°C and about 380°C for the proposed structural rearrangements in $Ba(OH)_2$, noted in the DSC trace for $Ba(OH)_2$ alone. The endotherm at approximately 380°C was followed by complex, but reproducible, overlapping exothermic and endothermic processes and a shift in the base line. The products of this complex

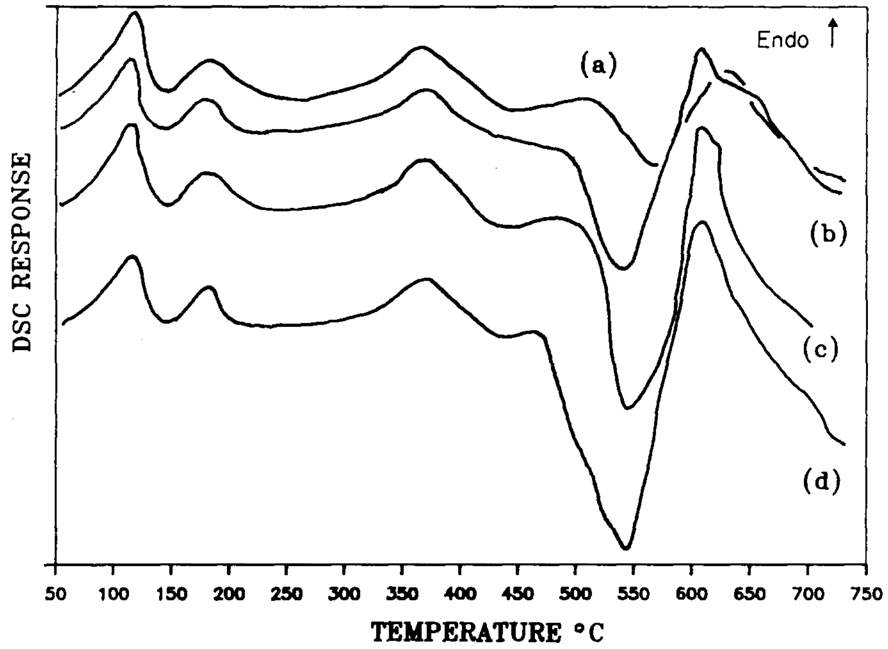

Fig. 5. DSC traces for different compositions of Mo/BaO_2 heated at 20°C min^{-1} in N_2. Curve a, 20% Mo; curve b, 30% Mo; curve c, 40% Mo; curve d, 50% Mo.

interaction underwent a further exothermic reaction at higher temperatures (≈560°C) giving an enthalpy change of -69 ± 5 J g^{-1}.

Mo/BaO_2 system

Compositions containing from 20 to 70% molybdenum sustained combustion [27]. The DSC trace for 40% Mo/BaO_2 (Fig. 5) recorded in N_2 with a heating rate of 20°C min^{-1} and sample masses of about 20 mg showed, in addition to the low temperature loss of water from BaO_2, a small endotherm, onset about 350°C, which was observed in the DSC trace of BaO_2 (Fig. 1) and was assigned to a structural rearrangement in $Ba(OH)_2$ prior to decomposition. This endotherm was followed by a large exotherm with variable onset temperature (≈490°C), probably caused by the main pyrotechnic reaction, which appeared to be superimposed on the decomposition endotherm of BaO_2. The enthalpy change was -830 ± 28 J g^{-1}.

The DSC traces of 20, 30 and 50% compositions of Mo/BaO_2 heated in N_2 at 20°C min^{-1} are also included in Fig. 5. The main exotherm increased in size as the proportion of fuel increased and the onset temperature decreased, thus decreasing overlap of the exotherm with the following endotherm.

Similar masses of 40% Mo/BaO_2 were heated at different rates between 5 and 160°C min^{-1} in the DSC. Some of the resulting traces are shown in

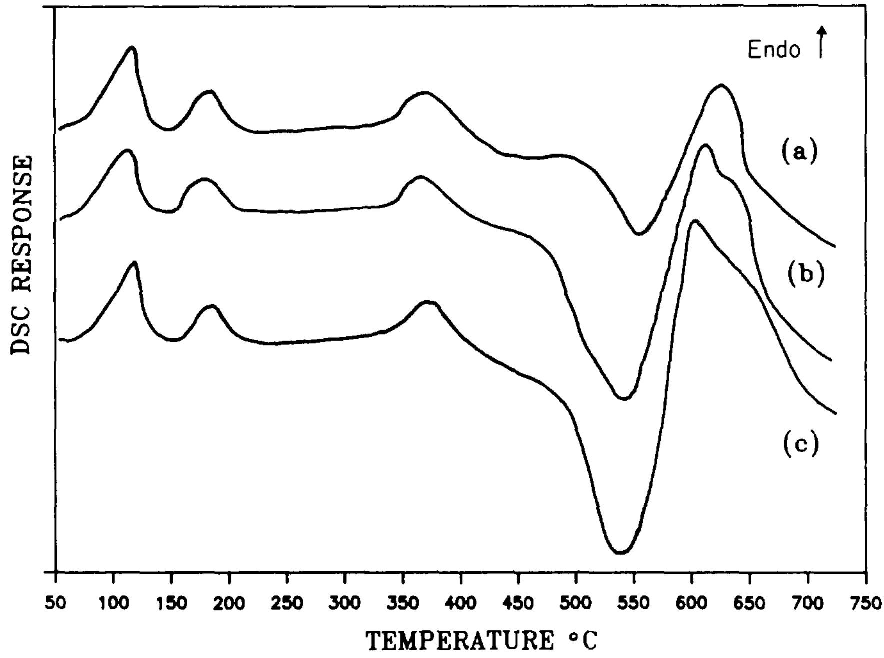

Fig. 6. Effect of heating rate on the DSC trace for 40% Mo/BaO_2 in N_2. Curve a, 5°C min^{-1}; curve b, 40°C min^{-1}; curve c, 80°C min^{-1}.

Fig. 6. The onset temperature of the main exothermic reaction was lowered as the heating rate was increased and the size of the endotherm increased.

The DSC trace for 40% Mo/BaO_2 in O_2 was similar to that in N_2 at the lower temperatures. Beyond approximately 500°C there was a general exothermic drift making the determination of the onset of the large and incomplete exotherm ($\Delta H \approx -70$ J g^{-1}) difficult to determine. The oxidation of molybdenum alone in O_2 (Fig. 2) started at about 600°C.

The TG trace for 40% Mo/BaO_2 heated in O_2 showed a mass gain of $8.0 \pm 0.1\%$ starting at about 470°C. This onset temperature corresponds approximately (≈440°C) to the mass gain attributed to the oxidation of the molybdenum powder by O_2 (Fig. 2).

Mn/SrO_2 system

Compositions containing from 20 to 80% manganese sustained combustion [27]. Samples of 40% Mn/SrO_2 heated at 20°C min^{-1} in N_2 in the DSC (Fig. 7), showed the low temperature endothermic loss of adsorbed water from SrO_2, followed beyond about 380°C by a large exotherm probably due to the pyrotechnic reaction between manganese and SrO_2. This exotherm appeared to be superimposed on the two endotherms at about 440° and at about 500°C resulting from the two-stage thermal decomposition of the unreacted SrO_2 (Fig. 1).

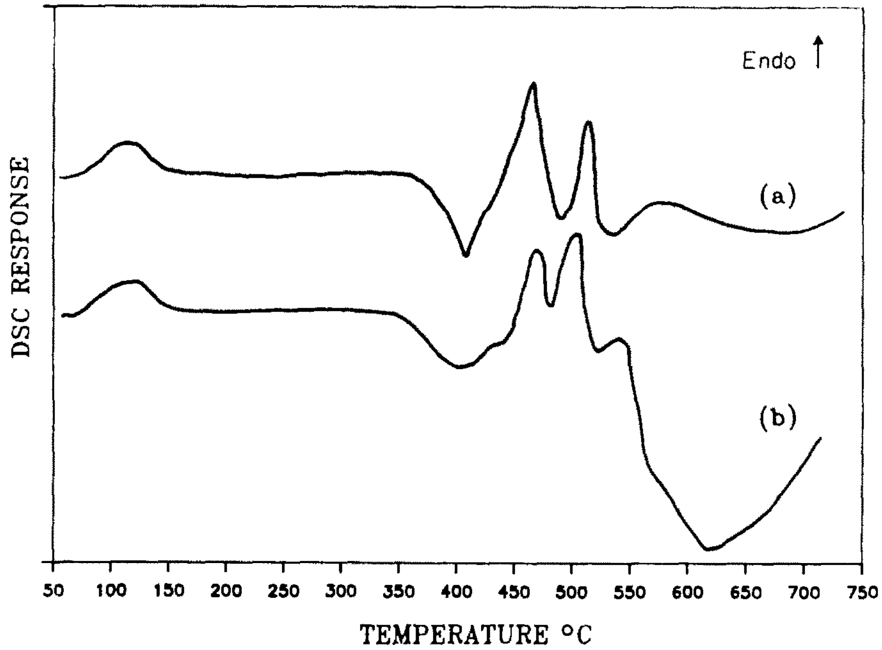

Fig. 7. DSC traces for 40% Mn/SrO_2 heated at 20°C min^{-1}. Curve a, in N_2; curve b, in O_2.

The DSC trace of 40% Mn/SrO_2 heated in O_2 (Fig. 7) was similar to that in N_2. Above 550°C there was a large, incomplete exotherm in the trace due to the oxidation of unreacted manganese. The DSC trace of manganese alone heated in O_2 (Fig. 2) showed that oxidation started at about 560°C. The TG trace in O_2 showed a mass loss (onset about 400°C) indicating decomposition of the oxidant prior to oxidation of the fuel.

As the composition of the Mn/SrO_2 system was changed from 20 to 50% manganese, the size of the endotherms at about 440 and 500°C (Fig. 8) decreased.

The Mo/SrO_2 system

Only two of the selected compositions, 40% and 45% molybdenum, sustained combustion [27]. Samples of various compositions (20–50% Mo) of the Mo/SrO_2 system were heated in N_2 in the DSC and even with large sample masses (up to 35 mg) and fast heating rates (up to 160°C min^{-1}) no reproducible exothermic events were observed in the resulting DSC traces. One experiment, using a covered pan containing only about 18 mg of 40% Mo/SrO_2 heated at 40°C min^{-1}, gave a small exotherm with onset temperature of about 580°C corresponding to an enthalpy change of -4 J g^{-1}. The second decomposition endotherm for SrO_2 was absent from this trace.

In the DSC trace for 40% Mo/SrO_2 in O_2, the onset temperatures of the endotherms caused by the decomposition of SrO_2 were increased

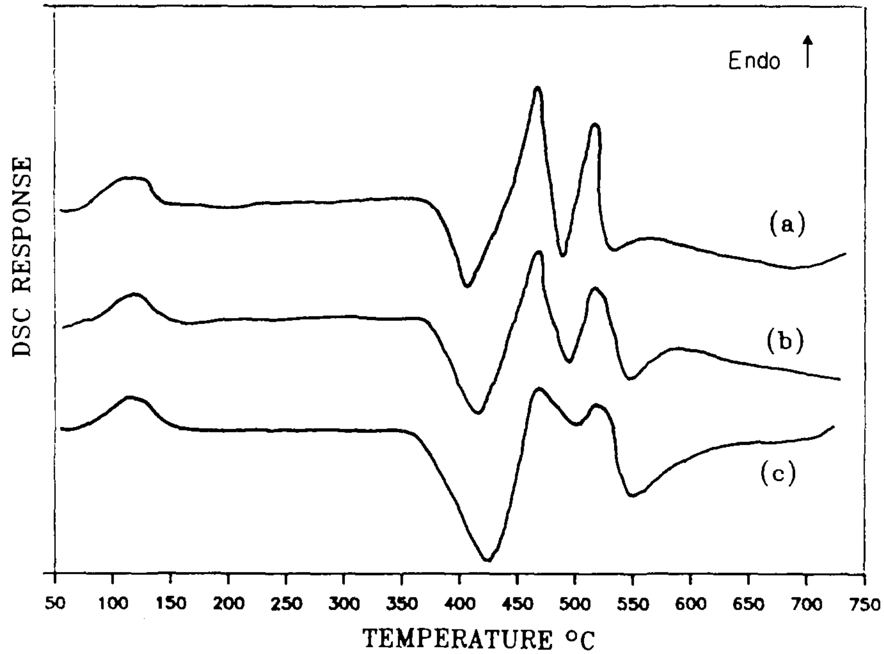

Fig. 8. DSC traces for different compositions of Mn/SrO_2 heated at 20°C min^{-1} in N_2. Curve a, 20% Mn; curve b, 30% Mn; curve c, 50% Mn.

slightly. A large exotherm with onset at about 660°C and enthalpy change of -635 ± 141 J g^{-1} was associated with the incomplete oxidation of molybdenum by the carrier gas (compare with Fig. 2).

Thermal analysis of the ternary pyrotechnic systems

Barium peroxide/strontium peroxide mixtures

A DSC trace for a 1:1 (by mass) mixture of BaO_2 and SrO_2 heated in N_2 at 20°C min^{-1} showed all six endotherms observed in the DSC traces for the individual oxidants (Fig. 1). All the processes associated with the individual constituents thus occur in the mixture without significant interference. The TG showed a multi-stage mass loss starting at about 385°C and a total mass loss of 21.1 ± 1.8% of the original sample mass. The expected mass loss for the decomposition of both peroxides is 23%.

Manganese/molybdenum mixtures

The DSC trace for a mixture of equal masses of manganese and molybdenum heated in N_2, showed only the allotropic phase change in manganese.

Mixed oxidant systems

$Mn/BaO_2/SrO_2$ system. The DSC trace for the 30:35:35 composition of $Mn/BaO_2/SrO_2$ heated in N_2 at 20°C min^{-1} (Fig. 9) showed the low

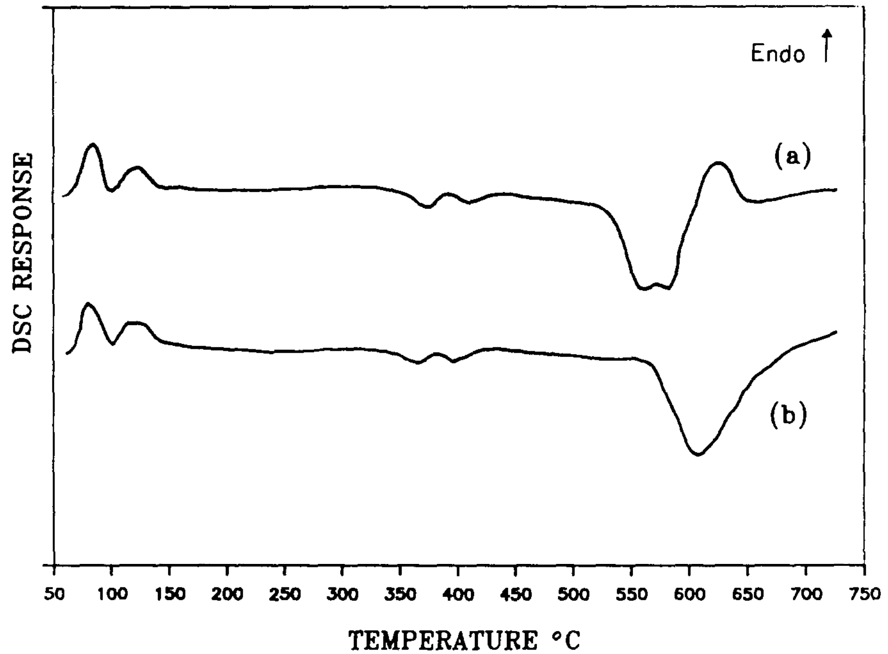

Fig. 9. DSC traces for 30:35:35% Mn/BaO_2/SrO_2 heated at 20°C min^{-1}. Curve a, in N_2; curve b, in O_2.

temperature endotherms associated with the loss of adsorbed water from BaO_2 and SrO_2, followed by a small exotherm ($\Delta H = -5 \pm 1$ J g^{-1}) with onset at about 360°C which was observed in the traces for the Mn/BaO_2 system (Fig. 3) and which has been associated with the rearrangement in $Ba(OH)_2$. The onset temperatures of the next two exotherms correspond approximately to the temperatures of the two endothermic stages for the decomposition of SrO_2. The small exotherm with onset at about 400°C was probably due to the reaction initiated by the first-stage of decomposition of the SrO_2 (about 390°C for SrO_2 and about 400°C in the BaO_2/SrO_2 mixture) while the large exotherm ($\Delta H = -86 \pm 10$ J g^{-1}) with onset about 500°C was initiated by the second-stage (about 535°C for SrO_2 and about 520°C in the BaO_2/SrO_2 mixture). The endotherm starting at about 580°C, probably due to the decomposition of unreacted BaO_2 which occurs at 600°C in BaO_2 and at 585°C in the BaO_2/SrO_2 mixture, was superimposed on the large exotherm (onset ≈500°C).

On changing the carrier gas to O_2, the higher temperature region of the DSC trace (Fig. 9) showed one broad exotherm at temperatures above 560°C due to the oxidation of manganese by the carrier gas superimposed on the process observed in N_2. The oxidation of manganese by O_2(g) occurs at about 560°C in the DSC (Fig. 2).

Mo/BaO_2/SrO_2 system. The DSC trace for 30:35:35 Mo/BaO_2/SrO_2 heated in N_2 at 20°C min^{-1} (with sample mass of about 20 mg) is shown in

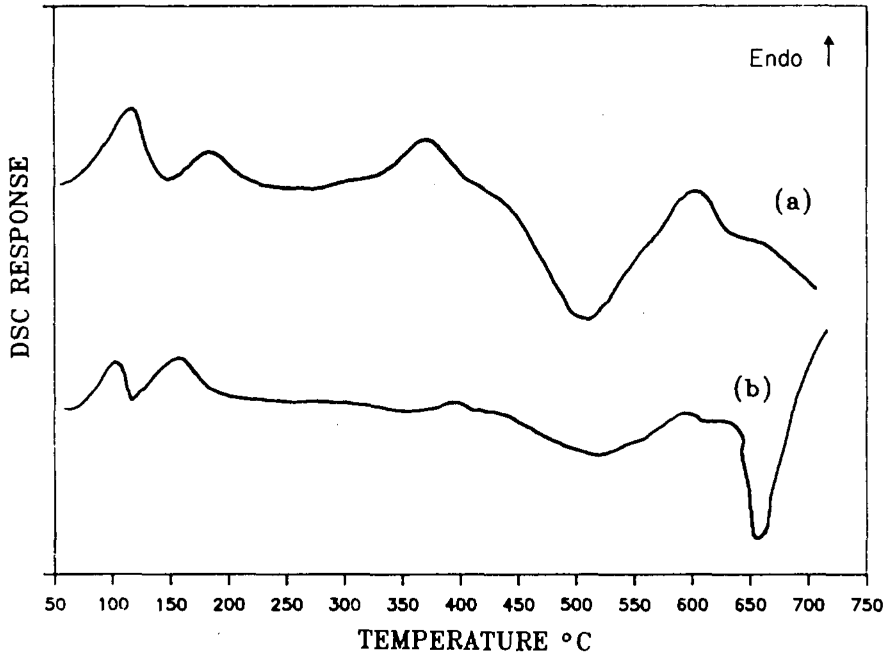

Fig. 10. DSC traces for 30:35:35% Mo/BaO_2/SrO_2 heated at 20°C min^{-1}. Curve a, in N_2; curve b, in O_2.

Fig. 10. As in the DSC traces for the Mo/BaO_2 binary system (Fig. 5) the endotherm assigned to the rearrangement in $Ba(OH)_2$ with onset at approximately 365°C was followed closely by a large exotherm (onset at about 430°C and $\Delta H = -81 \pm 6 \text{ J g}^{-1}$) due to the reaction between molybdenum and BaO_2. This exotherm masks the region in which decomposition of SrO_2 occurs, but there is some endothermic contribution (≈580°C) towards the end of the exotherm which could be due to the second stage of SrO_2 decomposition (onset ≈535°C, Fig. 1) or decomposition of BaO_2 (onset ≈600°C, Fig. 1).

In O_2, the DSC trace (Fig. 10) for this composition showed the small exotherm (onset ≈450°C) assigned to the reaction between molybdenum and BaO_2 (Fig. 5). This was followed by some endothermic activity probably due to the second stage of SrO_2 decomposition (onset ≈535°C, Fig. 1). As in the DSC trace for BaO_2 (Fig. 1), the decomposition of BaO_2 was not observed in the temperature range of the DSC due to the high partial pressure of O_2. The oxidation of molybdenum by the carrier gas was indicated by a large exotherm with onset at approximately 620°C (compare with Fig. 2).

The TG trace in N_2 showed a mass loss starting at about 400°C and corresponding approximately to the proposed reaction between molybdenum and BaO_2. Since there was a mass loss, any reaction must be preceded, accompanied, or followed by the decomposition of unreacted

SrO_2. Since the observed mass loss (5.1 ± 0.1%) was less than the expected mass loss (23%) for complete decomposition of the oxidants, some peroxide was consumed in the reaction.

The TG trace in O_2 showed a similar mass loss (onset ≈450°C) followed by a mass gain (onset ≈600°C). Molybdenum heated alone in O_2 was oxidized above 440°C. Decomposition of at least SrO_2 thus occurs before oxidation of molybdenum.

Mixed fuel systems

Mn/Mo/BaO₂ system. The DSC trace for 15:15:70 Mn/Mo/BaO_2 heated in N_2 at 20°C min^{-1}, sample mass about 20 mg, is shown in Fig. 11. The small exotherm with onset at about 390°C, observed in the traces for the Mn/BaO_2 system (onset 365°C, Fig. 3), was present. The reaction which caused the next exotherm, with onset at about 425°C, was probably not initiated by the endothermic decomposition of BaO_2, which was expected at higher temperatures (≈600°C). This behaviour was similar to that shown in the DSC traces (Fig. 5) for the Mo/BaO_2 system (exotherm onset at about 490°C). The next large exotherm (onset ≈500°C) overlaps the temperature range (≈600°C) of the decomposition of the unreacted BaO_2 and hence there may be some endothermic contribution to the complex exotherm associated with the oxidation of both fuels.

In O_2, the DSC trace for Mn/Mo/BaO_2 (Fig. 11) was similar to that in

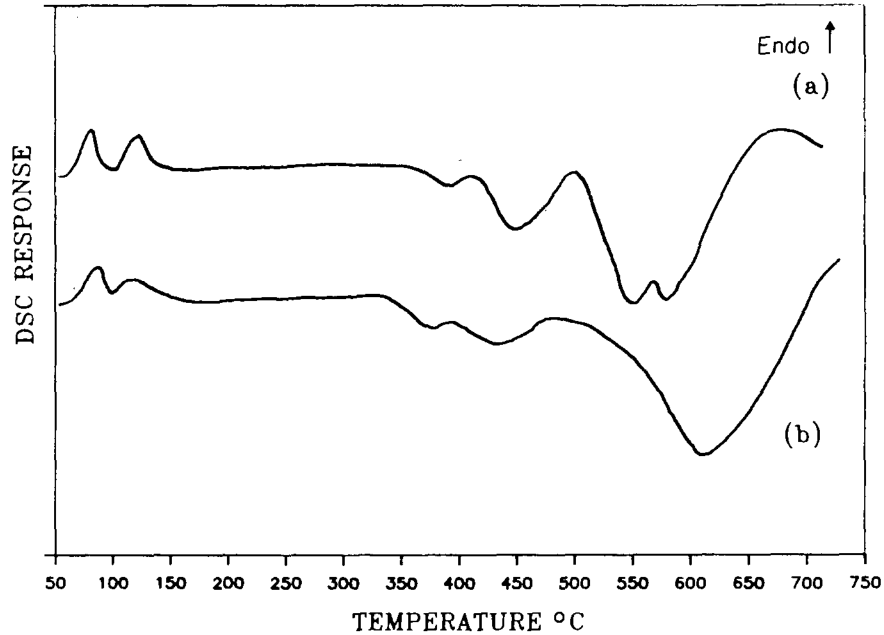

Fig. 11. DSC traces for 15:15:70% Mn/Mo/BaO_2 heated at 20°C min^{-1}. Curve a, in N_2; curve b, in O_2.

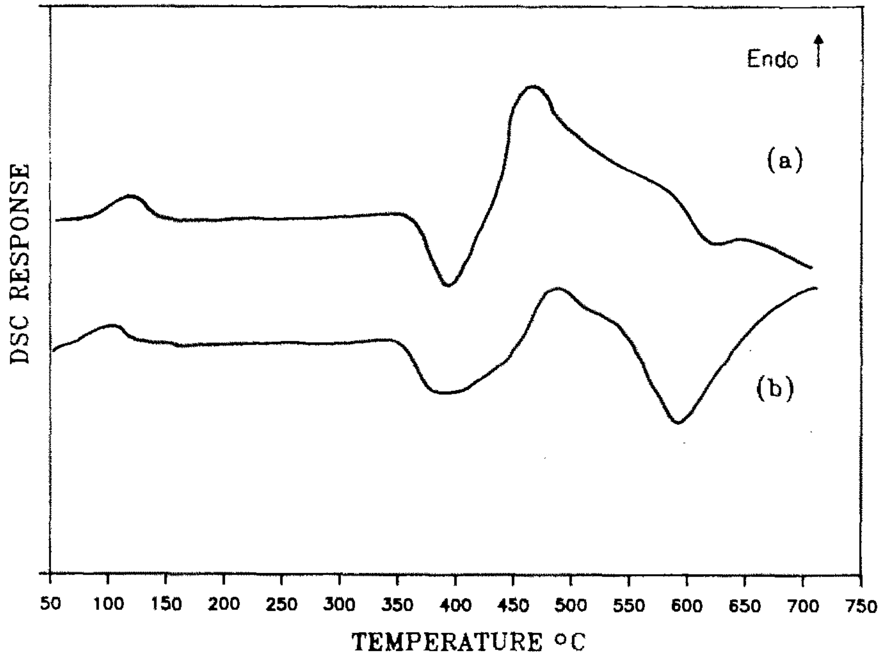

Fig. 12. DSC traces for 15:15:70% Mn/Mo/SrO_2 heated at 20°C min^{-1}. Curve a, in N_2; curve b, in O_2.

N_2 except that the third exotherm (onset ≈500°C) was broad and not resolved into the contributions seen in N_2. There is thus a contribution from the oxidation of both metals by the carrier gas.

Mn/Mo/SrO_2 system. The DSC trace for 15:15:70 Mn/Mo/SrO_2 heated in N_2 at 20°C min^{-1}, sample mass approximately 20 mg, is shown in Fig. 12. The exotherm at about 375°C corresponded approximately to the exotherm (380°C) observed in the DSC trace for the Mn/SrO_2 system (Fig. 7) which was assigned to the bulk reaction between manganese and SrO_2. The large endotherm at about 430°C ($\Delta H = 186 \pm 48$ J g^{-1}) was probably due to the decomposition of the unreacted SrO_2 observed in both the Mn/SrO_2 (onset ≈440°C, Fig. 7) and Mo/SrO_2 (≈400°C) systems. There was an exotherm at temperatures beyond the decomposition of SrO_2, i.e. with an onset temperature of about 575°C and with an enthalpy change of -28 ± 8 J g^{-1}. The onset temperature of this exotherm corresponded approximately to the onset temperature of the exotherm at about 580°C in the DSC trace for the Mo/SrO_2 binary system and was thus probably due to a reaction between molybdenum and SrO_2 promoted by manganese.

The DSC trace in O_2 was similar to that in N_2 to beyond the first exotherm (onset ≈370°C). This exotherm was followed by the endothermic initial decomposition of unreacted SrO_2 and a larger broad exotherm corresponding to the oxidation of the residual metals by the carrier gas (≈550°C).

The TG trace for $Mn/Mo/SrO_2$, heated in O_2 at 20°C min^{-1}, showed a slight mass gain (<1% of the original mass) at about 320°C. At about 410°C the mass loss of 7.1 ± 0.1% due to the decomposition of SrO_2 was observed with the characteristic step at approximately 465°C. This was followed by a mass gain at about 610°C assigned to the interaction between the newly formed products and O_2 gas.

CONCLUSIONS

Individual reactants

Barium peroxide may contain absorbed water and also traces of hydroxide and carbonate as impurities. No evidence of melting was observed and endothermic decomposition to BaO(s) and O_2(g) occurs above 600°C and is fairly reversible on cooling in air.

Strontium peroxide may also contain absorbed water and possibly hydroxide and carbonate impurities. Decomposition occurs in two endothermic stages, the first above about 400°C and the second at above about 530°C. No intermediate other than SrO_2(s) was identified.

The powdered metals, manganese and molybdenum, react readily on heating in O_2(g) in the DSC above 500°C (Mn) and above 600°C (Mo). In the more open sample configuration of the TG, these onset temperatures were lowered to 350°C (Mn) and 450°C (Mo). The reactivity of the metal powders caused problems in that it was difficult to flush all traces of oxidizing gases from the thermobalance housing. MoO_3 sublimes above about 750°C, in O_2, in the TG.

Two binary pyrotechnic systems containing BaO_2

Mn/BaO_2 system

The proposed endothermic rearrangement in $Ba(OH)_2$ at about 360°C appeared to initiate an exothermic reaction between manganese and BaO_2. The large and incomplete exotherm at about 660°C appears to be initiated by the onset of peroxide decomposition. A solid–solid reaction between manganese and BaO_2 cannot be ruled out since the TG trace showed no mass loss. Following previous suggested mechanisms [8, 9], the first process (≈360°C) could be a pre-ignition reaction followed by bulk oxidation at 660°C. The DSC trace for 40% $Mn/Ba(OH)_2$ did not show an exotherm so the presence of peroxide is probably also required.

Mo/BaO_2 system

Only one exotherm was observed in the DSC trace for this system. The endothermic rearrangement in the $Ba(OH)_2$ impurity, which was suggested to initiate the pre-ignition reaction in the Mn/BaO_2 system, was not associated with an exotherm in the Mo/BaO_2 system. The main exothermic reaction between molybdenum and BaO_2 at about 490°C is well below the temperature required for the onset of decomposition of the peroxide. The unreacted BaO_2 undergoes decomposition at higher temperatures which affects the shape of the oxidation exotherm. The exothermic reaction was not accompanied by a mass loss and therefore it is suggested that, at least under the conditions of thermal analysis, the reaction could be between reactants in the condensed phase, assuming that any gases involved had sufficient time to escape the solid material and thus change the sample mass. The metal fuel may also catalyze the decomposition of the oxidant.

An increase in the proportion of fuel, up to a composition of 50% Mo/BaO_2, caused the main reaction to start at lower temperatures. Increasing the heating rate also lowered the onset temperatures of the main reaction exotherms.

Two binary pyrotechnic systems containing SrO_2

Mn/SrO_2 system

Only one exothermic reaction (onset ≈380°C) was observed in the DSC traces of Mn/SrO_2 in both N_2 and O_2. This exotherm is overlapped by the first of the two endothermic stages of decomposition of unreacted SrO_2. The onset temperature of this proposed reaction between manganese and SrO_2 was altered by changes in the composition of the Mn/SrO_2 system. It is not possible from thermal analysis to distinguish between reaction of manganese with $SrO_2(s)$ or with $O_2(g)$ formed in the early stage of decomposition of SrO_2.

In O_2, the large exotherm at about 550°C due to the oxidation of unreacted manganese by the atmosphere showed that some fuel remained unreacted in the 40% composition and that it was available (i.e. not protected by a layer of product) for reaction with the $O_2(g)$ under the conditions of thermal analysis.

Mo/SrO_2 system

The Mo/SrO_2 mixture differed from the other three binary systems in that for no composition of Mo/SrO_2 could an exotherm due to the reaction between molybdenum and SrO_2 be produced reproducibly under the conditions applying in the DSC. The one example of exothermic activity in a DSC trace of Mo/SrO_2 was at temperatures above the decomposition of SrO_2 (≈580°C), compared to (≈380°C) for the Mn/SrO_2 system.

Ternary systems

Thermal analysis of the BaO_2/SrO_2 mixture indicated that there was no interaction between the two oxidants as they were heated to 950°C. All the thermal events observed could be interpreted solely in terms of the events observed for the individual oxidants. Similarly, the thermal behaviour of the ternary pyrotechnic systems could also be explained quantitatively in terms of their constituent binary systems.

Both of the mixed oxidant systems showed the low temperature loss of water from both oxidants. The $Mn/BaO_2/SrO_2$ system showed a low temperature ($\approx$365°C) exotherm, which, as for the Mn/BaO_2 system, was attributed to a pre-ignition reaction between manganese and BaO_2. This reaction was initiated by the proposed endothermic rearrangement of the $Ba(OH)_2$ impurity. The $Mo/BaO_2/SrO_2$ system did not show a corresponding pre-ignition reaction and the endotherm due to the rearrangement of the $Ba(OH)_2$ in the DSC trace was not obscured by an exotherm. The trace was similar to that for the Mo/BaO_2 system. The DSC traces for the two mixed oxidant systems were dominated by the fuel/BaO_2 contributions.

Thermal analysis of the Mn/Mo mixture indicated that there were no interactions between the two fuels as they were heated to 950°C. The existence of a pre-ignition reaction was again observed in the $Mn/Mo/BaO_2$ system, initiated by the proposed rearrangement of the $Ba(OH)_2$ impurity. Reaction in the ternary system was dominated by the reactions between manganese and BaO_2. The DSC trace of the $Mn/Mo/SrO_2$ system was a combination of the DSC traces of the two binary systems.

General remarks

Pyrotechnic reactions may be studied under the controlled conditions of thermal analysis and under the less-controlled conditions of ignition [27]. Depending on the conditions of the thermal analysis experiments (i.e. sample mass, heating rate, etc.), ignition of a pyrotechnic sample may or may not occur during the heating programme. In this way the main thermal events of a pyrotechnic mixture or its separate constituents in the presence of either an inert or reactive atmosphere may be identified and characterized.

Kinetic parameters derived from suitable thermal analysis experiments are discussed in Part 3 of this series [31] together with parameters derived from combustion experiments [27].

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