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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60^{th} birthday

REACTIONS OF POWDERED SILICON WITH SOME PYROTECHNIC OXIDANTS

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Thermogravimetry (TG) and differential scanning calorimetry (DSC) have been used to examine the thermal behaviour, in N_2 and in air, of the Si/Sb_2O_3, Si/KNO_3, Si/Fe_2O_3 and Si/SnO_2 pyrotechnic systems, in relation to the behaviour of the individual constituents.

TG curves for Si powder, heated alone in air, showed that limited oxidation of Si occurred above 700°. In N_2, Sb_2O_3 sublimed completely between 500 and 900° and, in air, sublimation was accompanied by oxidation to Sb_2O_4. The Sb_2O_4 decomposed at higher temperatures. DSC curves for KNO_3 heated in N_2 showed the usual crystalline transition and melting endotherms followed by endothermic decomposition between 400 and 950°. DSC and TG curves of SnO_2 and Fe_2O_3 revealed no thermal events when samples were heated to 1000° in either N_2 or air.

For the Si/Sb_2O_3 system, the oxidation of Si by Sb_2O_3 between 590 and 700°, was complicated by sublimation of Sb_2O_3 in N_2 and also by the oxidation of Sb_2O_3 in air. No thermal events were observed for the Si/SnO_2 and Si/Fe_2O_3 systems when heated under a variety of conditions in either N_2 or in air, although these systems do sustain combustion on suitable ignition. In the Si/KNO_3 system, oxidation of Si occurs in a KNO_3 melt at temperatures above 560° in nitrogen and in air.

Silicon powder is extensively used as a solid fuel in pyrotechnic reactions. The most thoroughly studied silicon-containing binary pyrotechnic systems are Si/Pb_3O_4 [1-4], Si/PbO_2 [5] and Si/PbO [1, 6, 7]. Other initially solid oxidants that have been used in binary combinations with Si as fuel, include Fe_2O_3 [8], KNO_3 [9-11], SnO_2 [12, 13] and $BaSO_4$ [14, 15]. Some ter-

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nary systems with two oxidants [16, 17] or an additional fuel [5, 18], as well as systems with ferrosilicon (FeSi) [19-21] and calcium silicide ($CaSi_3$) [22] have been described.

A fundamental question which arises in pyrotechnic reactions [23] is whether reaction is a genuine solid–solid reaction, a solid–liquid reaction involving either a molten fuel, or a molten oxidant, or whether the fuel reacts only with gaseous oxygen (or some other gaseous species) formed by the prior thermal decomposition of the oxidant, or whether some combination of these processes contributes to the overall reaction.

The oxidation of silicon by gaseous oxygen has been studied in detail [24-32]. Reaction occurs at relatively high temperatures (990 to 1200°) which are still well below the melting point of Si (1410°). The SiO_2 product is usually amorphous [28, 29] (m.pt. quartz 1610° $\rightarrow$ tridymite 1703° $\rightarrow$ cristobalite 1723° $\rightarrow$ SiO_2 (l)). Oxidation is accelerated in the presence of water vapour and the formation of Si–O–H bonds is reported [25]. Oxidation occurs primarily at the Si/SiO_2 interface and O_2 therefore has to diffuse through the oxide layer for reaction to occur [26].

Reaction between silicon and gaseous nitrogen occurs [33] at higher temperatures (~1400°) than in oxygen.

In this study, the thermal behaviour of several binary pyrotechnic systems containing Si as the fuel and oxidants other than lead oxides, has been examined using DSC and TG. These systems were chosen on the basis of (a) their ability to sustain combustion, and (b) the requirement that their maximum combustion temperatures should be <1700°, which is the limit for temperature measurement with noble–metal thermocouples. The combustion processes have been examined in detail [34], and the main features of the combustion of the binary systems are summarized in Table 1.

Table 1 Combustion of binary silicon–containing pyrotechnic system

System	Range of compositions which sustain combustion, % Si by mass	Range of burning rates, $cm \cdot s^{-1}$	T_{max},, °C	–q* $kJ \cdot g^{-1}$
Si/Sb_2O_3	20 to 50	0.16 (20%) to 0.87 (35%)	1250	0.60 (43%)
Si/Fe_2O_3	20 to 40	0.23 (20%) to 0.45 (40%)	1250	0.83 (30%)
Si/SnO_2	20 to 55	0.51 (20%) to 1.70 (40%)	1370	0.60 (45%)
Si/KNO_3	10 to 90	0.17 (30%) to 3.45 (80%)	–	–

* Heat output estimated from T_{max} and the heat capacity of the composition

The processes which occur during combustion of a pyrotechnic composition may be far removed [35] from those which may be identified during thermal analysis experiments, where the samples are small and the experimental conditions are such that thermal runaway [36] may be avoided.

Experimental

Materials

The silicon and KNO_3 used in this study were obtained from AECI Explosives and Chemicals Ltd., Sb_2O_3 from Merck, Fe_2O_3 from Baker Analysis, and SnO_2 from BDH.

All constituents were sieved through a 53 μm sieve before mixing. Compositions were mixed by brushing through a 75 μm screen. The mixed compositions were then stored in air–tight containers.

Apparatus

A Perkin–Elmer TGA–7 thermobalance and PE 3700 data station, calibrated against the Curie points of nickel, perkalloy and iron, was used for this study. The upper temperature limit of the TG furnace is 1000°. Both uncompacted and compacted samples with sample masses from 0.2 to 10 mg, in standard platinum pans without lids, were heated at rates of 20 $\text{deg}\cdot\text{min}^{-1}$ (unless otherwise stated) in nitrogen and in air (flow rate 4 $\text{ml}\cdot\text{min}^{-1}$, inlet pressure 20 kPa).

DSC studies were carried out, under similar conditions, in a Perkin–Elmer DSC–7 with samples in platinum pans with lids. The DSC was calibrated against the melting points of indium and zinc. The upper temperature limit of the DSC is 730°.

The thermoanalytical results were complemented by infrared spectra of solid products in KBr disks.

All thermal analysis results shown are the mean of from three to five runs and errors are calculated from range estimates of the results.

Results and discussion

Thermal behaviour of silicon powder

DSC curves of silicon powder heated in N_2 showed no significant thermal event up to ~700°. TG curves showed a slight mass loss of 0.2±0.1% between 50 and 700° due, probably, to the desorption of surface impurities. The sample began to gain in mass above 700°, probably due to slow reaction of silicon with residual traces of oxygen in the purge gas, and this gain was still continuing at the upper temperature limit of 1000°. It is unlikely that this gain in mass was due to the nitridation of silicon since this reaction, to form Si_3N_4, is reported [33] to occur at temperatures greater than 1200°.

The infrared spectrum of a sample of untreated silicon showed a weak absorption band between 1300 and 1000 cm^{-1} due to SiO_2 which is formed as a result of the spontaneous surface oxidation of silicon on exposure to oxygen.

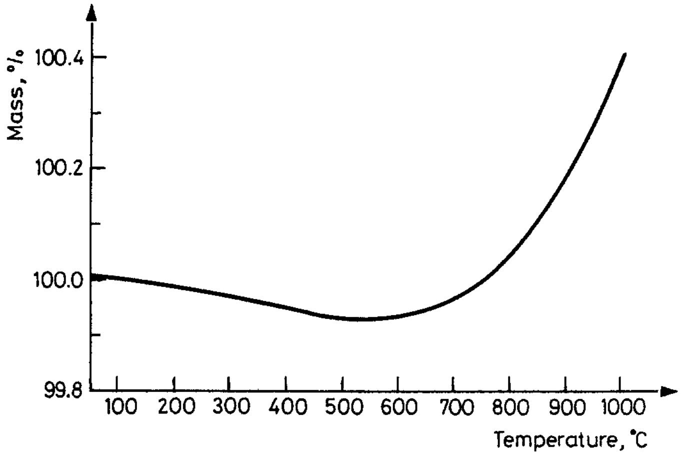

Fig. 1 TG curve for silicon powder heated at 10 deg·min^{-1} in air

The TG curves of samples of silicon, heated to 1000° in air, (Fig. 1), showed a mass loss, similar to that observed in nitrogen, of 0.2±0.1% up to 660°. A gain in mass starting at ~700°, similar to that in nitrogen, confirmed the sensitivity of the powder to oxidation above ~600°. The infrared spectrum of the product showed a main peak at 1230 cm^{-1} and a shoulder between 1100 and 1000 cm^{-1} (peak at 1070 cm^{-1}) due to SiO_2.

DSC curves of silicon, heated to 720° in air, showed no significant thermal event. This upper limit is just near the onset of slow oxidation in the TG runs.

Thermal behaviour of the oxidants

Sb_2O_3

When Sb_2O_3 was heated to 1000° in N_2 in platinum pans without lids (Fig. 2, curve a), a rapid mass loss of 91.2±1.0% occurred from 500 to 620°. A large portion of Sb_2O_3 therefore sublimed at temperatures below its melting point (656°). A further slower mass loss of 3.1±1.3%, occurred between 620 and 800°, in which the remainder of the Sb_2O_3 vaporized. The total mass loss over the temperature range 50 to 1000° was 97.8±1.6%.

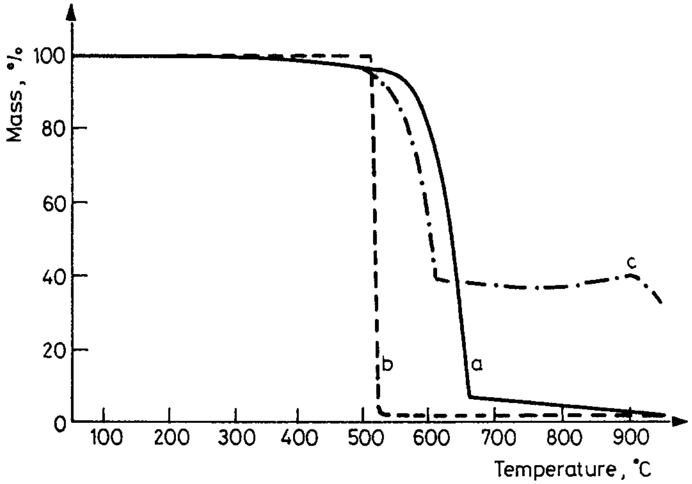

Fig. 2 TG curves for Sb_2O_3 (a) heated at 20 deg·min^{-1} in N_2 in open pan; (b) heated at 20 deg·min^{-1} in N_2 with lid; (c) heated at 20 deg·min^{-1} in air

On heating samples in sample pans with lids, a very rapid mass loss of 97.8±2.0% was observed between 520 and 580° (see Fig. 2, curve b).

The infrared spectrum of the untreated Sb_2O_3 compared well with that of cubic Sb_2O_3 with peaks at 820 and 380 cm^{-1} [37], as did the spectrum of a sample of the sublimed Sb_2O_3 which had collected on the cooler parts of the TG furnace.

The DSC curve for Sb_2O_3, heated in N_2 (Fig. 3, curve a), showed the expected broad endotherm between 300 and 580° due to sublimation of Sb_2O_3. This is followed by two not very reproducible endotherms at 624 and 681°.

The first endotherm is due to the cubic to orthorhombic crystalline transition of Sb_2O_3 and the second due to the melting of Sb_2O_3.

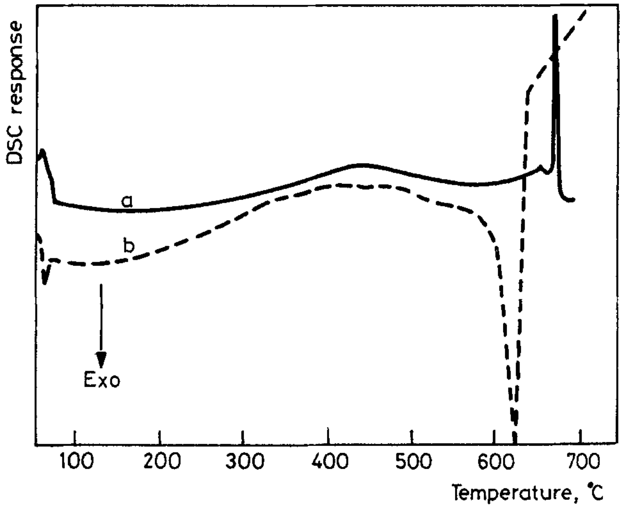

Fig. 3 DSC curve for Sb_2O_3; (a) heated at 20 deg·min^{-1} in nitrogen; (b) heated at 20 deg·min^{-1} in air

The DSC curve of Sb_2O_3 in air (Fig. 3, curve b), showed an exotherm between 500 and 650° due to the oxidation of Sb_2O_3 by gaseous oxygen

$$2Sb_2O_3(s) + O_2(g) \rightarrow 2Sb_2O_4(s)$$

The change in enthalpy for this reaction was –0.81±0.21 kJ (g of Sb_2O_3)$^{-1}$ compared to the expected value of –0.75 kJ (g of Sb_2O_3)$^{-1}$ ($\Delta H = -218$ kJ (mol of Sb_2O_3)$^{-1}$). This exotherm occurred in a similar temperature range to the mass loss due to sublimation observed in the TG traces, suggesting that, in air, sublimation and oxidation of Sb_2O_3 occur simultaneously.

The TG curve for Sb_2O_3 in air (Fig. 2, curve c), showed that the mass loss, ascribed to the sublimation of Sb_2O_3, began at ~ 510° but the loss of 63.3±2.9% was less than that (~92%) observed in nitrogen. The residue after this initial mass loss consisted of Sb_2O_3 and Sb_2O_4. After a further mass loss of 1.7±0.9% between 600 and 760°, a gain in mass of 3.8±1.1% (or 6.2±2.2% of the sample mass afetr initial mass loss) occurred between 760 and 900° (see Fig. 2, curve c). This gain in mass is due to the oxidation of unreacted Sb_2O_3 (expected gain in mass is 5.5% per g of Sb_2O_3). A further mass loss of between 12 and 27% occurred above 910° and this stage was incomplete at the upper temperature limit of 1000°. The onset of this mass loss corresponds to the decomposition of Sb_2O_4 (910°).

The infrared spectrum of the residue after heating to 1000° in air confirmed the formation of Sb_2O_4 with an absorption peak at 735 cm^{-1}, a shoulder at 760 cm^{-1}, and a peak at 635 cm^{-1}, with a shoulder at 670 cm^{-1}. Further Sb_2O_4 peaks occurred at 595, 525, 465 and 370 cm^{-1}. The formation of Sb_2O_5 during oxidation cannot be ruled out since [37] the infrared spectrum of Sb_2O_5 closely resembles that of Sb_2O_4.

TG and DTA curves of Sb_2O_3 in N_2 reported by Golunski *et al.* [37] showed that for cubic Sb_2O_3 (senarmontite) that mass loss which began at 640° was ~100% after heating to 1000° [37]. Agrawal *et al.* [38] reported however, that mass loss occurred at as low as 430°. The DTA curves for cubic Sb_2O_3 [37] showed an irreversible endotherm at 628° due to the cubic to orthorhombic (valentinite) phase transition. This was followed at ~640° by a reversible endotherm due to the melting of valentinite. Thermal analyses of orthorhombic Sb_2O_3 showed slightly different characteristics to cubic Sb_2O_3: only a reversible endotherm due to melting was observed at 643° and mass loss due to vaporization began at 625° and was ~90% after heating to 1000°. XRD analysis [37] showed that no chemical decomposition of Sb_2O_3 had occurred on being heated to 1000° in nitrogen.

There are conflicting reports about the thermal stability of Sb_2O_3 in air. According to Agrawal *et al.* [38], oxidation of cubic Sb_2O_3 occurs above 510° and proceeds in two stages. The gain in mass for the first stage between 510 and 600° was 4.5% (expected mass gain for complete oxidation was 5.9%). The second stage between 630 and 670° showed a mass gain of ~1%. The authors claimed [38] that during the first stage, small quantities of orthorhombic Sb_2O_3 were formed at ~570°. The orthorhombic Sb_2O_3 was apparently more stable than cubic Sb_2O_3, so the oxidation of the former occurs at 630°. The DTA curves of Golunski *et al* [37] showed that the oxidation of cubic Sb_2O_3 in air began only at 575°, while the oxidation of orthorhombic Sb_2O_3 was first noticeable at 463°. In the DSC traces of Sb_2O_3 in air, two exotherms (onset 337 and 442°) were also reported [39]. The first exotherm is due to the oxidation of the surfaces of Sb_2O_3. Oxidation of the bulk occurred at a higher temperature during the second exotherm.

Fe_2O_3

TG curves of Fe_2O_3, heated in either nitrogen or in air, showed a small almost linear mass loss of ~0.6 between 60 and 940°. DSC traces in N_2 and in air showed no significant thermal event below the limit of 720°.

The infrared spectrum of Fe_2O_3 had a broad absorption band with a peak at 535 cm^{-1}, a sharp peak at 475 cm^{-1}, a weak sharp peak at 380 cm^{-1} followed by a strong band with peak at 335 cm^{-1}. There was no change in the infrared spectrum of a sample of Fe_2O_3 (m.p. 1565°) after it had been heated to 1000° and cooled.

SnO_2

TG curves of SnO_2, heated in N_2 and in air, showed only an approximately linear mass loss of ~1% which was incomplete by 1000°. No thermal event was observed in the DSC traces of SnO_2 (m.pt. 1630°) in nitrogen or in air. The infrared spectrum of the residue compared well with that of untreated SnO_2 and showed a strong broad multiplet between 750 and 370 cm^{-1}, a strong sharp peak at 320 and a sharp peak at 265 cm^{-1}.

KNO_3

In the TG curve for KNO_3, heated in N_2 (see Fig. 4, curve a), decomposition occurred above 500° in two partially-overlapping stages (500 to 770° and 770 to 1000°). The mass loss between 500 and 770° was 72.0±1.2% and 14.0±1.0% between 770 and 1000°.

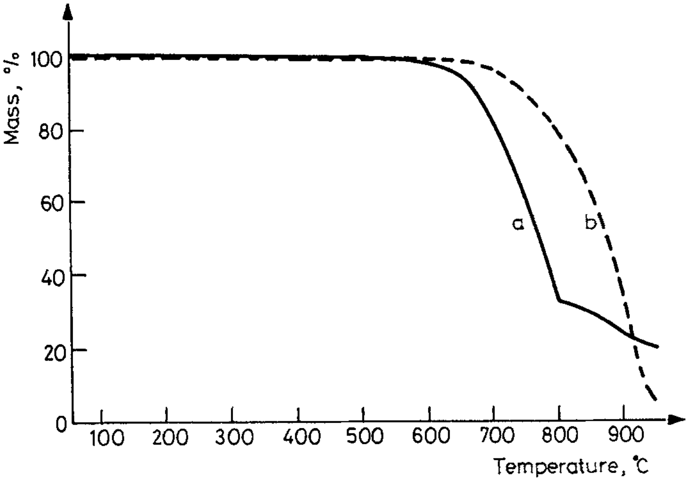

Fig. 4 TG curves for KNO_3; (a) heated at 20 deg·min^{-1} in N_2; (b) heated at 20 deg·min in air

According to Freeman [40], decomposition occurs between 650 and 750° to the nitrite, followed at 800° by

$$2KNO_2(l) \rightarrow K_2O(l) + 2NO(g) + O_2(g)$$

while, according to Serotkin [41], K_2O is not formed until 1000° and decomposition is only complete above 1200°. The mass of the residue in N_2 (12.1±1.8% of the original) is less than expected for K_2O and supports reports of volatilization of K_2O (m.p. 380°).

In the TG curves for KNO_3 heated in air, decomposition occurred above 500° and proceeded through a rapid mass loss (84.8±1.2%) between 500 and 920°. The two-stage mass loss observed in N_2 was not resolved in the trace for KNO_3 in air (see Fig. 4, curve b). The total mass loss in air of 91.9% was greater than the 85% observed in air.

The DSC curves of KNO_3 in N_2 (20 deg·min^{-1}) (Fig. 5, curve a) and air (10 deg·min^{-1}) (Fig. 5, curve b) were similar, confirming the onset of endothermic decomposition at about 500° after the rhombic-to-trigonal crystalline phase transition at 116° and melting at 325°.

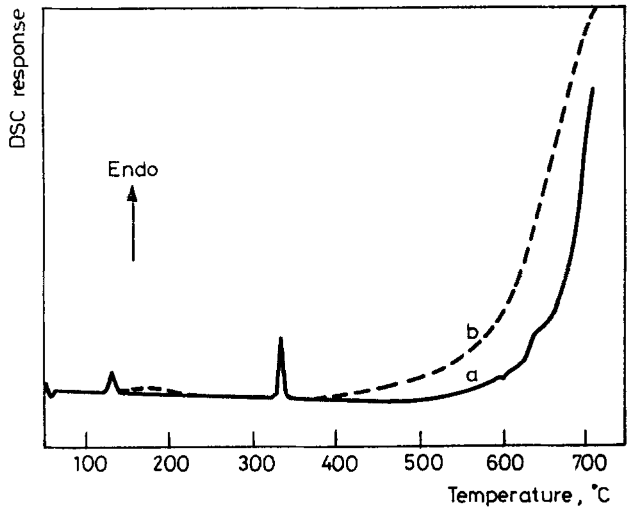

Fig. 5 DSC curves for KNO_3; (a) heated at 20 deg·min^{-1} in N_2; (b) heated at 10 deg·min^{-1} in air

The individual oxidants, described above, behaved very differently on heating. Fe_2O_3 and SnO_2 showed very little change over the temperature range accessible (<1000°). Neither melted or decomposed in an inert atmosphere, or oxidized significantly in air. Sb_2O_3 sublimed readily and may also melt and/or oxidize further in air. KNO_3 melted at relatively low temperatures (325°) and decomposed readily in the melt. With these differences in behaviour, the oxidants, on binary combination with silicon as fuel, could be expected to show significant differences in reactivity.

Thermal behaviour of the binary Si/oxidant systems

All the binary Si systems sustain combustion over a range of compositions and reached similar maximum temperatures (~1300°) during approximately adiabatic combustion, but had different linear burning rates (see Table 1).

Si/Sb_2O_3 compositions

In the DSC traces of a 40% Si/Sb_2O_3 composition in nitrogen, (Fig. 6, curve a), an exotherm from 590 to 615° with a change in enthalpy of -0.53 ± 0.13 kJ·g^{-1}, was observed. This exotherm occurred in the temperature range during which sublimation of Sb_2O_3 occurred when it is heated alone. If the reaction

$$3Si(g) + 2Sb_2O_3(g) \rightarrow 3SiO_2(s) + 2Sb(s) \qquad (1)$$

is assumed to occur during this exotherm, the change in enthalpy, calculated from standard enthalpies of formation, would be -1.82 kJ·g^{-1}.

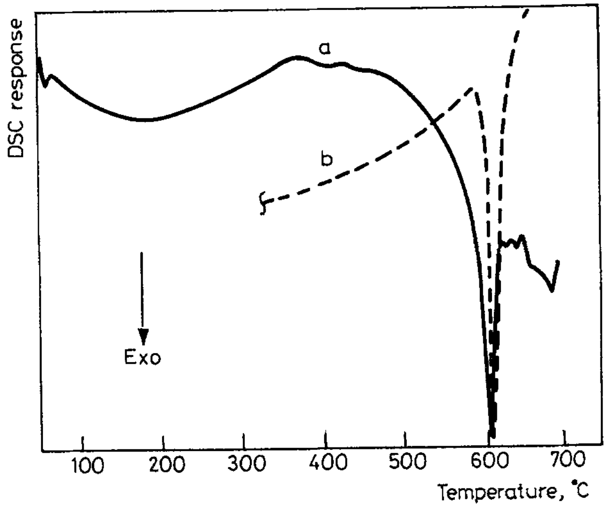

Fig. 6 DSC curves for 40% Si/Sb_2O_3; (a) heated at 20 deg·min^{-1} in N_2; (b) heated at 10 deg·min^{-1} in air

DSC curves of the above composition in air (Fig. 6, curve b) showed an exotherm between 600 and 680° and the change in enthalpy was -0.74 ± 0.19 kJ·g^{-1}. This exotherm occurred in a similar temperature range to that in which the sublimation and oxidation of Sb_2O_3 was observed in air (Fig. 3, curve b).

The TG traces for the 40% Si/Sb_2O_3 composition heated to 1000° in N_2 in platinum pans without lids (Fig. 7, curve a), showed a mass loss of 48.5±0.4% between 420 and 630° followed by a further loss of 8.5±1.5% between 650 and 995°. Calculations based on TG mass-losses showed that only <5% of the total silicon had reacted with Sb_2O_3 compared to the expected 46.5%.

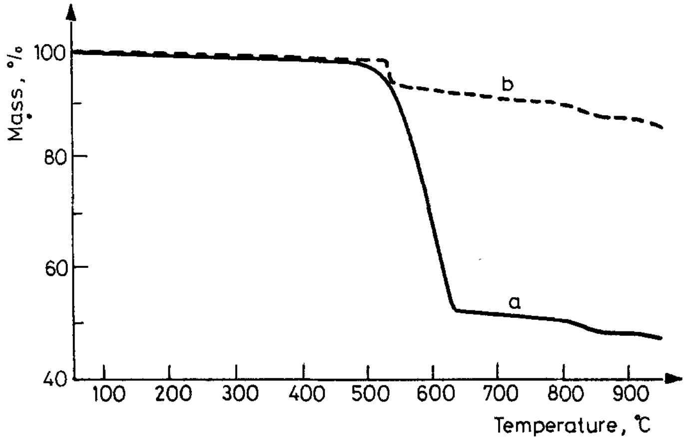

Fig. 7 TG curves for 40% Si/Sb_2O_3; (a) heated at 20 deg·min^{-1} in N_2 no lids; (b) heated at 20 deg·min^{-1} in N_2 with lids

When the sample pans were covered with lids (see Fig. 7, curve b) the mass loss was only 6.1±0.3% over the temperature range 520 to 570°, followed immediately by a slower mass loss of 3.6±0.4% (580 to 995°). Only ~20% of the total silicon had reacted despite attempts at preventing the escape of Sb_2O_3 vapour. The presence of SiO_2 was detected in the infrared spectrum of the residue.

The TG curve of 40% Si/Sb_2O_3 in air in platinum pans without lids, (Fig. 8, curve a), showed that sublimation begins at ~410°. The mass loss observed between 410 and 610° was 43.4±2.8%. This region of rapid mass loss was followed by a slower mass loss of 1.2±0.5% over the temperature range 610 to 900°. Between 910 and 1000° a slight and not very reproducible mass loss of ~1%, due to the decomposition of Sb_2O_4, was observed. When the sample pans were covered with lids, the rapid mass loss of 10.5±2.3%, was observed between 470 and 700° (Fig. 8, curve b).

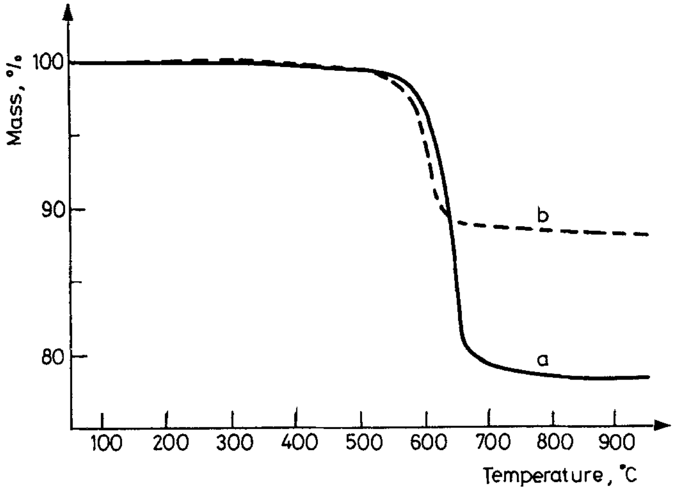

Fig. 8 TG curves for 40% Si/Sb_2O_3; (a) heated at 20 deg·min^{-1} in air no lids; (b) heated at 20 deg·min^{-1} in air with lids

DSC traces of the above composition, heated at various heating rates in nitrogen and in air, showed an exotherm over the range 580 to 620°. Enthalpy values measured from these DSC curves (Table 2) were not very reproducible and varied according to mass of the sample and the heating rate used. The changes in enthalpy measured for the composition in air are generally greater than those observed in nitrogen as a result of a contribution made by the reaction of Sb_2O_3 with gaseous O_2. For mixtures heated in nitrogen, maximum ΔH was reached at 20 deg·min^{-1} with no further increase with increased heating rate. The infrared spectrum of the residue after heating to 1000° showed the presence of SiO_2 and trace amounts of the oxidant.

Table 2 ΔH values measured from the DSC traces of a 40% Si/Sb_2O_3 composition heated nitrogen and in air

Heating rate, °C·min^{-1}	ΔH, kJ·g^{-1}	
	Nitrogen	Air
10	0.21±0.10	0.61±0.14
20	0.53±0.13	0.74±0.19
50	0.43±0.20	0.93±0.19
100	0.46±0.14	0.61±0.14

Expected change in enthalpy for a 40% Si/Sb_2O_3 composition is –1.37 kJ·g^{-1}

Si/Fe_2O_3 compositions

On heating samples of loose powders of a 35% Si/Fe_2O_3 composition to 1000° in nitrogen, or in air, the slow mass loss, over the range 50 to 1000°, of 0.6±0.2% was similar to that observed on heating Fe_2O_3 alone. The infrared spectrum of the residue showed only the strong presence of Fe_2O_3. DSC curves in nitrogen and also in air showed no thermal event over the temperature range of the instrument. Similar results were obtained when compacted samples were examined and also when either the heating rate ($\leq$150 $\text{deg}\cdot\text{min}^{-1}$) or the sample mass (<30 mg) was varied. Thus the process responsible for propagation of combustion of this composition could not be readily initiated under the conditions applying, and within the temperature limits of the thermal analysis equipment.

Si/SnO_2 compositions

The TG curves a 30% Si/SnO_2 composition in nitrogen, or in air, showed a slight mass loss (1.5±0.6%) over the range 50 to 1000°. The DSC trace, in N_2 and in air, showed no thermal event between 50 and 720°. Increasing the heating rate ($\leq$150° $\text{deg}\cdot\text{min}^{-1}$) or the sample mass (<30 mg) did not result in any exothermic reaction.

The infrared spectrum of the residues after heating in nitrogen and in air, showed only the characteristic absorption bands of SnO_2.

Again it was not possible to initiate a self–sustaining reaction in this composition, as loose powders or as compacted pellets, under typical thermoanalytical conditions.

Si/KNO_3 compositions

A typical TG curve for a 30% Si/KNO_3 mixture, heated at 20 $\text{deg}\cdot\text{min}^{-1}$ in N_2, (Fig. 9, curve a) showed a single mass loss of 23.3±0.8%. The extent of the loss and the temperature range over which the loss occurs, varied with composition [9] of the mixture as shown in Table 3. However, the onset temperature for this mass loss, which varied within narrow limits between 560 and 575° for the compositions examined, appeared to be independent of composition.

A DSC curve for 30% Si/KNO_3, heated at 10 $\text{deg}\cdot\text{min}^{-1}$ in N_2, is shown in Fig. 10. The crystalline and melting transitions of KNO_3 are evident, as is the onset of endothermic decomposition of KNO_3 (~500°). Upon this endotherm is superimposed a strong exothermic spike at ~660°, characteristic of ignition.

Table 3 Summary of TG and DSC data for the Si/KNO_3 system heated in nitrogen

Si,	TG		DSC		$-\Delta H$,
%	Temp. range, °C	mass loss, %	Temp. range, °C	$-\Delta H$, $kJ \cdot g^{-1}$	$kJ \cdot g^{-1}$
20	570 to 950	36.8±2.6	–	–	4.22
30	570 to 910	23.3±0.8	660 to 680	0.97±0.02	4.09
40	565 to 860	17.3±2.0	640 to 680	2.39±0.03	3.51
50	570 to 790	11.7±0.8	600 to 720	1.90±0.04	2.92
60	560 to 760	10.7±0.6	600 to 710	1.00±0.02	2.34
70	560 to 690	7.6±0.4	620 to 650	0.43±0.02	1.75
80	575 to 653	4.5±0.4	570 to 620	0.34±0.03	1.17

*Calculated from standard enthalpies of formation, based on. Eq. 2.

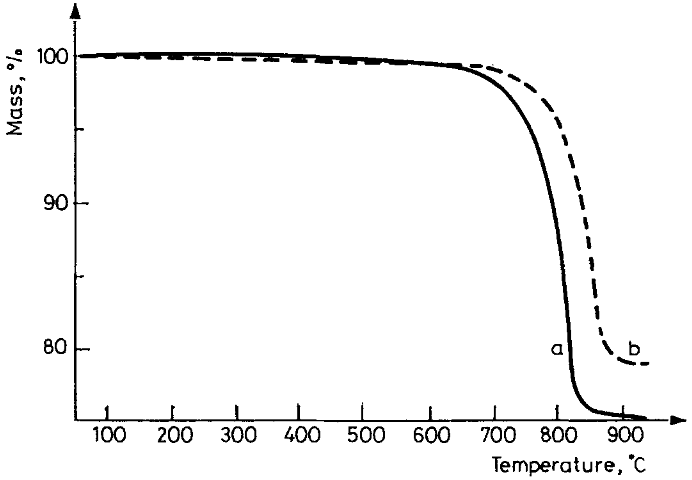

Fig. 9 TG curves for 30% Si/KNO_3; (a) heated at 20 deg·min^{-1} in N_2; (b) heated at 20 deg·min^{-1} in air

When the proportion of Si in the composition was increased, the resulting DSC curve for a sample in nitrogen showed a similar sharp exo-therm at ~600°. The onset temperature of the exotherms varied between 570 and 640° and generally occurred within the same temperature range as the mass loss observed in the TG curves. If it is assumed that the reaction which occurs during this exotherm is

$$2Si(s) + 2KNO_3(l) \rightarrow 2SiO_2(s) + K_2O(l) + N_2(g) + 0.5O_2(g) \qquad (2)$$

the enthalpy of reaction determined from standard enthalpies of formation is –4.3 $kJ\cdot g^{-1}$ (or –590.7 kJ (mol of $KNO_3)^{-1}$). The maximum enthalpy of reaction, determined from DSC traces, was –2.29 $kJ\cdot g^{-1}$ and occurred at approximately 40% Si (see Table 3).

Table 4 Summary of TG and DSC data for the Si/KNO_3 system heated in air

Si, %	TG		DSC	
	Temp. range, °C	mass loss, %	Temp. range, °C	$-\Delta H$, $kJ\cdot g^{-1}$
20	560 to 960	35.2±1.2	570 to 650	0.72± 0.01
30	570 to 930	20.7±0.2	–	–
40	560 to 850	14.9±0.1	–	–
50	540 to 750	12.9±0.1	–	–
60	540 to 720	10.9±0.4	570 to 700	1.64± 0.01
70	580 to 720	6.9±0.2	570 to 660	1.16± 0.02
80	550 to 670	5.4±0.1	570 to 640	0.66±50.03

The TG curve of a 30% Si/KNO_3 composition in air (Fig. 9, curve b) showed a single mass loss. The extent of the mass loss depended upon the composition of the mixture and generally decreased with decreasing proportion of oxidant (see Table 4). The DSC curves of the above composition showed the usual endothermic transitions. The onset of the exothermic reaction between the decomposing oxide and solid silicon occurred at ~600°

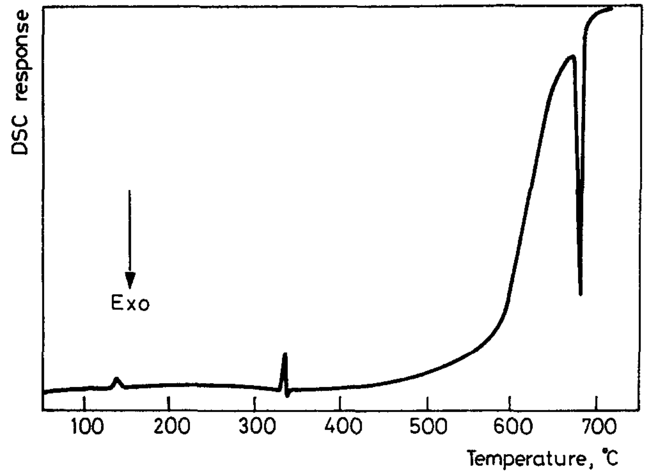

Fig 10 DSC curve for 30% Si/KNO_3 heated at 10 $deg\cdot min^{-1}$ in N_2

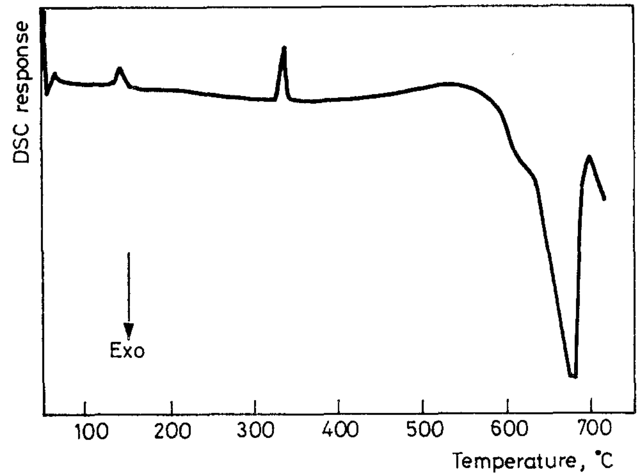

Fig. 11 DSC curve for 60% Si/KNO3 heated at 20 deg·min^{-1} in air

and was incomplete at 720°, which is the upper temperature limit of the instrument. For a given composition, the ΔH in air (Table 4) appears to be greater than that observed in nitrogen (Table 3) possibly as a result of a contribution to reaction made by atmospheric O_2. A broad exotherm was observed between 570 and 700° (Fig. 11), for a 60% Si/KNO_3 composition.

Conclusions

Thermal analyses of several pyrotechnic mixtures with silicon as fuel have been carried out using thermogravimetry (TG) and differential scanning calorimetry (DSC) as principal techniques. All of the mixtures had been shown [34] to propagate combustion after suitable ignition. The reactions which occur during thermal analysis are not, however, always identical to those which occur under the conditions of ignition, because of different temperature-time histories. The information obtained from thermal analysis can however, provide some insight into the reaction mechanisms which occur during the burning of pyrotechnic compositions.

Oxidation of silicon powder, heated on its own in air only became detectable above 700°.

The individual oxidants behaved very differently on heating. Fe_2O_3 and SnO_2 showed no thermal events on heating on their own in either N_2 or air. KNO_3 melts at relatively low temperatures (325°) and decomposes in the melt at above 500°. Sb_2O_3 sublimes readily and may also melt. Simultaneous oxidation to Sb_2O_3 occurs in air.

The Si/Fe_2O_3 and the Si/SnO_2 systems showed no significant thermal activity in the temperature range studied and under the conditions of thermal analysis (sample masses <30 mg and heating rates $\leq$150 deg·min^{-1}). Maximum reaction temperatures recorded during the combustion of these mixtures (see Table 1) were well below the melting points of Fe_2O_3 (1565°), SnO_2 (1630°) and silicon (1410°). The reactions in these systems thus appear to occur predominantly between solid oxidant and solid fuel. Even when compositions were compacted, ignition could not be induced in the TA equipment.

A highly exothermic reaction between the decomposing molten KNO_3 and silicon occurs from ~550°. The temperature range in which this exotherm occurs depends on the composition of the mixture. The changes in enthalpy measured for the various mixtures heated in air indicated that there was an exothermic contribution to reaction from gaseous oxygen.

Some reaction between Si and Sb_2O_3 occurs during the sublimation of Sb_2O_3. Loss of Sb_2O_3 vapour may be decreased by using sample pans with lids. In air, the reaction of silicon with Sb_2O_3 is further complicated by simultaneous oxidation of Sb_2O_3 by gaseous oxygen.

Burning rates for each of the binary systems (Table 1) increased as the proportion of silicon in the composition increased (within limits). This is consistent with control by the amount of fuel oxidised.

The relative increase in rate was greatest within the Si/KNO_3 system and the highest absolute rate was that of the 80% Si/KNO_3 system which may be expected for good contact of a molten oxidant over a large surface of fuel. Suprisingly, though, the next highest burning rate was that of 40% Si/SnO_2 and the burning rates for the Si/SnO_2 system are generally higher than those for the other 'inert' oxidant, Fe_2O_3.

The increase in burning rate of the Si/Sb_2O_3 system with proportion of fuel could be expected from consideration of the ease of escape of subliming Sb_2O_3.

More quantitative discussion of the influence of the oxidant will be provided in the light of detailed analysis of the temperature profiles for combustion [34].

References

1 A. Z. Moghaddam and G. J. Rees, Fuel, 60 (1981) 629.
2 S. S. Al-Kazraji, M. S. Doulah and G. J. Rees, Fuel, 60 (1981) 598.
3 S. Nakahara and T. Hikita, J. Ind. Explos. Soc. Japan, 21 (1960) 9.
4 T. J. Hedger, Propellants Explos. Pyrotech., 8 (1983) 95.
5 J. W. Mclain, "Pyrotechnics", Franklin Institute Press, Philadelphia, Pennsylvania, 1980.
6 S. S. Al-Kazraji and G. J. Rees, J. Thermal Analysis, 16 (1979) 35.
7 J. A. C. Goodfield and G. J. Rees, Fuel, 64 (1985) 1627.
8 H. Goldschmidt, US Patent No. 906009, 1908.
9 G. Krishnamohan, E. M. Kurian and K. R. K. Rao, 8th Int. Pyro. Sem., (1982) 404.
10 T. T. L. Leeuw, Report No. RN 0861/A, Technical Dept., AECI Ltd., 1988.
11 T. T. L. Leeuw, Report No. RN 0839/A, Technical Dept., AECI Ltd., 1988.
12 UK Patent No. GB 2 084 984 A, 1980.
13 J. A. C. Goodfield and G. J. Rees, Fuel, 60 (1981) 151.
14 A. L. Davitt and K. A. Yuili, UK Patent No. GB 2 089 336, 1980.
15 G. Kelly, CXA Technical Report No. IR-99-003, CXA Canada, 1984.
16 S. R. Yoganarasimhan and O. S. Josyulu, Def. Sci., J., 37 (1987) 73.
17 S. R. Yoganarasimhan, J. Thermal Anal., 34 (1985) 937.
18 S. L. Howlett and F. G. J. May, Thermochim. Acta, 9 (1974) 213.
19 S. Nakahara, J. Ind. Explos. Soc. Japan, 22 (1961) 259.
20 S. Nakahara, J. Ind. Explos. Soc. Japan, 20 (1959) 356.
21 L. Sulacsik, J. Thermal Anal., 5 (1973) 33.
22 A. Jarvis, Combust. Flame, 14 (1970) 313.
23 J. E. Spice and L. A. K. Staveley, J. Soc. Chem. Ind., 68 (1949) 313, 348.
24 N. Mott, "Condution in Non-Crystalline Materials", Oxford University Press, 1987.
25 S. Rigo, F. Rochet, B. Agius and A. Straboni, J. Electrochem. Soc., 129 (1982) 867.
26 B. E. Deal and A. S. Grove, J. App. Phys., 36 (1965) 3770.
27 E. Rosencher, A. Straboni, S. Rigo and G. Amsel, App. Phys. Lett., 34 (1979) 254.
28 J. C. Phillips, J. Non-cryst. Solids, 34 (1979) 153.
29 W. A. Tiller, J. Electrochem. Soc., 127 (1980) 619.
30 W. A. Tiller, J. Electrochem. Soc., 127 (1980) 625.
31 W. A. Tiller, J. Electrochem. Soc., 128 (1981) 689.
32 N. T. Cabrera and N. T Mott, Rep. Prog. Phys., 12 (1948) 163.
33 G Braun, G. Bowden, K. Henkel and H. Rossbach, J. Thermal Anal., 33 (1988) 479.
34 R. A. Rugunanan, PhD Thesis, Rhodes University, in preparation.
35 P. G. Laye and E. L. Charsley, Thermochim. Acta, 120 (1987) 329.
36 M. E. Brown, Thermochim. Acta, 148 (1989) 521.
37 S. E. Golunski, T. G. Nevell and M. I. Pope, Thermochim. Acta, 51 (1981) 153.
38 Y. K. Agrawal, A. L. Shashimohan and A. B. Biswas, J. Thermal Anal., 7 (1975) 635.
39 P. W. Centres, R. L. Wright, F. D. Price and C. J. Kelnke, Physics and Chemistry of Glasses, 30 (1989) 149.
40 E. S. Freeman, J. Amer. Chem. Soc., 79 (1957) 383.
41 G. D. Serotkin, Zh. Neorg. Khim., 4 (1959) 11.

Zusammenfassung — Mittels TG und DSC wurde das thermische Verhalten der pyrotechnischen Systeme Si/Sb_2O_3, Si/KNO_3, Si/Fe_2O_3 und Si/SnO_2 in N_2 und in Luft im Vergleich zum Verhalten der einzelnen Komponenten untersucht.

TG-Aufnahmen über das Erhitzen von Si-Pulver in Luft zeigten eine begrenzte Oxidation von Silizium oberhalb 700°C. Sb_2O_3 sublimiert in Stickstoff vollständig zwischen 500 und 900°C, in Luft wird die Sublimation durch Oxidation zu Sb_2O_4 begleitet. Sb_2O_4 zersetzt sich bei höheren Temperaturen. DSC-Aufnahmen für KNO_3 in N_2 zeigen die gewohnten Umwandlungs- und Schmelzendothermen, gefolgt von einer endothermen Zersetzung zwischen

400 und 950°C. Die DSC- und TG-Kurven für SnO_2 und Fe_2O_3 zeigen bei Erhitzen bis 1000°C weder in N_2 noch in Luft den Verlauf thermische Prozesse an.

Bei dem System Si/Sb_2O_3 spielt sich neben der Oxidation von Si durch Sb_2O_3 zwischen 590 und 700°C auch eine Sublimation von Sb_2O_3 in N_2 sowie eine Oxidation von Sb_2O_3 in Luft ab. Für die Systeme Si/SnO_2 und Si/Fe_2O_3 konnten durch Erhitzen unter einer Reihe von Bedingungen weder in Luft noch in N_2 Thermoprozesse nachgewiesen werden, obwohl diese Systeme nach geeigneter Zündung den Brennvorgang aufrechterhalten. Im System Si/KNO_3 erfolgt sowohl in N_2 als auch in Luft oberhalb 560°C die Oxidation von Si in der KNO_3-Schmelze.