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Review

THERMAL ANALYSIS OF PYROTECHNICS *

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ABSTRACT

Thermal analysis is used widely in the study of pyrotechnics as a routine test facility and as a research tool. Its impact on our understanding of reaction mechanisms has been particularly significant. The present review provides an account of experimental techniques and considers selected areas of application. It is illustrative rather than exhaustive with references restricted to the readily available open literature.

CONTENTS

1. INTRODUCTION

The application of thermal analysis to pyrotechnics is a relatively small and specialized field of activity. Even so, it has had a significant influence

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* This review is concerned with differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

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on our understanding of the mechanism of pyrotechnic reactions. These reactions produce heat, light or smoke for use in a variety of devices. A description of pyrotechnics and their applications is given in refs. 1–3. Traditionally the components of pyrotechnics have been finely divided solids but current practice makes increasing use of resin-bonded and polymeric materials. Metallic and a few non-metallic elements and organic substances are used as fuels with oxides and oxysalts as oxidants. In this review, we are not concerned with the thermal analysis of the components per se even though such an investigation would play an important part in the study of pyrotechnics. The increasing availability of high temperature thermal analysis equipment has added impetus to the study of pyrotechnics where reactions may occur at temperatures above 1000 °C. The evaluation of the hazard potential of pyrotechnics by means of thermal analysis has been recommended. This forms an area of work which in its more general application outside pyrotechnics has become of increasing importance in view of the growing emphasis on occupational safety. Although other reviews have contained a limited number of references to the thermal analysis of pyrotechnics, there does not seem to have been a major review devoted entirely to the subject. The pioneering studies at Picatinny Arsenal, U.S.A., were discussed by Freeman and Rudloff [4] and Krien [5]. Collins and Haws [6] have included references to some pyrotechnics in their broader review of the thermochemistry of explosives. More recently, Conkling [7] has described the various uses of DTA in the study of pyrotechnics and explosives. The present review is meant to be illustrative rather than exhaustive in its account of the work which has appeared in the open literature.

The interpretation of thermal analysis curves for pyrotechnics needs to be approached with care. Under conditions which lead to ignition, a sharp exotherm is obtained in which the measured temperature rise may be several hundred degrees. Although the temperature of ignition may be obtained, the mechanism relates to the thermal analysis environment and is unlikely to be the same as that for ignition by a hot wire or fuse. The temperature thus obtained may vary significantly according to the experimental conditions. Where ignition does not occur, several peaks are usually obtained, and it is under these conditions that DTA and DSC have proved to be of particular value. In combination with other techniques it has been possible to identify reaction stages. X-ray diffraction, IR spectroscopy, optical and electron microscopy are all techniques which have been applied. Such reaction stages may not be entirely the same as those which occur in the ignited sample since the temperature–time histories are very different. However, as a starting point for investigating the macroscopic features of pyrotechnic reactions the techniques of thermal analysis have proved to be invaluable.

2. EXPERIMENTAL METHODS

Perhaps the most important single factor to be borne in mind is the hazardous nature of pyrotechnics. There is the obvious danger of accidental ignition since many mixtures are sensitive to friction and electrical discharge. Equally there is the danger of inhalation of finely divided components many of which are toxic. The preparation and handling calls for the utmost care. Small samples are often best prepared by brush-mixing the components through a fine sieve. The design of the thermal analysis experiments should take into account the violent nature of pyrotechnic reactions which when "gassy" can cause products to be widely scattered, possibly resulting in damage to the thermal analysis head. The likelihood of such damage exists even with some designs of modern equipment but the use of small samples, made possible by high instrumental sensitivity, has reduced the hazard potential.

2.1. General techniques

The study of pyrotechnics requires a careful choice of material for the crucible. Pyrex glass, quartz and platinum have been used most widely. The choice is often a compromise intended to minimize reaction between the crucible and either the different pyrotechnic components or their reaction products. Platinum itself is attacked not only by molten magnesium and aluminium but also by boron at high temperatures. Tall crucibles are necessary to retain samples such as those containing nitrates, nitrites and dichromates which foam or creep. With modern commercial equipment, sample masses are usually 2–50 mg. Small samples (10 mg or less) and low heating rates (equal to or lower than $5\,^{\circ}\mathrm{C}\ \mathrm{min}^{-1}$) are used for non-ignition experiments although the precise conditions are dictated by the nature of the pyrotechnic and the design of the specimen-holder assembly.

The specialized nature of pyrotechnics has led to a number of experimental refinements. Inert materials have been added to samples to reduce the violent nature of the reactions [8]. Jarvis [9] preferred to add the pyrotechnic components separately to the crucible to overcome the difficulty of obtaining representative samples when the components differ markedly in their particle size. For some pyrotechnics the high temperature peaks may be weak but attempts to resolve them by increasing the sample mass leads to ignition at a lower temperature. Such peaks can be studied by combining the intermediate products from several experiments with smaller samples [10]. Most experiments have been carried out with the sample in an inert atmosphere: helium, argon and nitrogen have been used. Due care is needed when selecting nitrogen since it reacts with some fuels at high temperatures. Some of the experiments reported with the sample in air have proved to be less satisfactory because identification of the pyrotechnic reactions has been obscured by the reaction between the fuel and atmospheric oxygen. In extreme cases the presence of oxygen has engendered ignition of the sample. Titanium in an ancillary crucible may be used to remove traces of oxygen from the sample-holder assembly. Alumina appears to have been used most frequently as the reference material but in a number of papers explicit information is not given.

2.2. Specialized equipment

A number of researchers have described equipment which has been purpose-built often with specialized measurements in mind. Perhaps the most celebrated is the DTA apparatus described by Gordon and Campbell [11,12] which was used extensively in the early work at Picatinny Arsenal (for examples, see refs. 13–15). Unusual by present day standards was the location of the thermocouples in the samples and the large mass of the samples themselves (1–5 g). Campbell and Beardell [16] developed a DTA apparatus in which the samples were confined to their initial volume (Fig. 1). This procedure has the merit of approaching the conditions under which many pyrotechnic mixtures are used. The effect of confinement was studied for a number of pyrotechnics but no common pattern of behaviour was observed. Beardell et al. [17] have described a high heating rate apparatus capable of raising the temperature of very small samples (50–200 μg) at rates up to 10^{6}°C min^{-1}. The samples were deposited on a platinum filament and the temperature monitored using an IR detector. The feasibility of the technique was demonstrated using calcium oxalate as a test

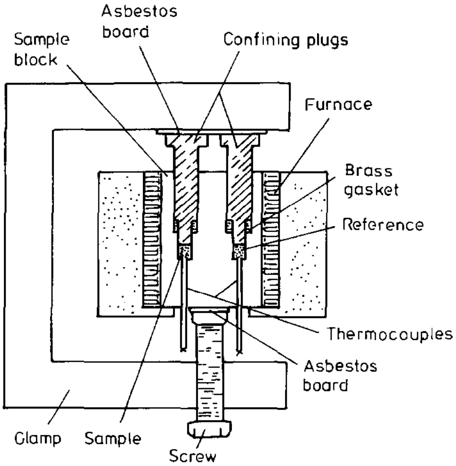

Fig. 1. DTA apparatus for constant-volume confinement of the sample. Reproduced from C. Campbell and A.J. Beardell, Thermochim. Acta, 8 (1974) 27.

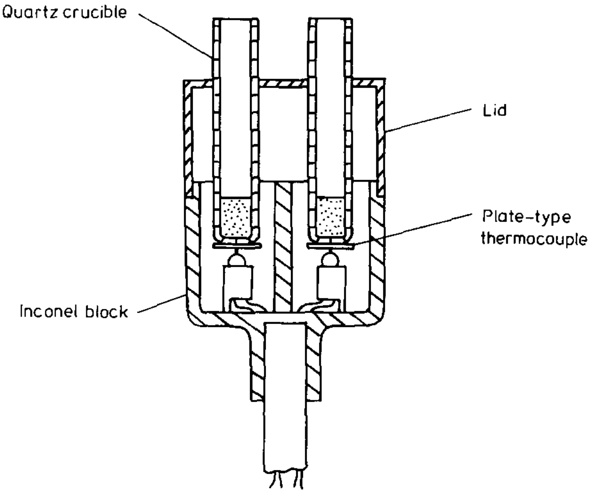

Fig. 2. DTA apparatus for ignition temperature measurements. Reproduced from E.L. Charsley, C.T. Cox, M.R. Ottaway, T.J. Barton and J.M. Jenkins, Thermochim. Acta, 52 (1982) 321.

sample. In principle at least, it offers the opportunity of studying pyrotechnic reactions at a temperature rise rate similar to that in the ignited sample.

An apparatus for the routine determination of ignition temperatures has been described by Charsley et al. [18]. A DTA head (Fig. 2) was designed to promote ignition by minimizing heat losses. Contamination of the thermocouples was largely eliminated, leading to reproducible temperature measurements over a large number of experiments without the need for frequent calibration. A photocell was introduced to detect ignition for those pyrotechnics which are ejected from the crucible giving rise to a poorly defined temperature trace. For further examples of the use of this apparatus, see refs. 19–21. Boddington et al. [22] have described the use of a modified DTA head to measure the thermal diffusivity of mixtures of tungsten and $K_2Cr_2O_7$. A disadvantage of the technique is that the samples need to be large (about 20 g) which for some materials would involve an unacceptable hazard.

3. SELECTED APPLICATIONS

Table 1 lists many of the pyrotechnics which have been studied by DTA and DSC. They include examples of flares, smokes, igniters and delays. The objective has been to gain an understanding of both the nature of pyrotechnic reactions and the ignition characteristics of the mixtures. The work by Gordon and Campbell [11] set the pattern for future developments. The DTA technique was one of comparison between the thermal analysis curves

TABLE 1

Some pyrotechnics studied by DTA and DSC

Pyrotechnic	Ref.	Pyrotechnic	Ref.	Pyrotechnic	Ref.	Pyrotechnic	Ref.
Al–		Fe/Si–MnO_2	33	*Si*–		*W*–	
$KClO_3$, $KClO_4$	73			PbO	32, 78	$K_2Cr_2O_7$	10
$KClO_4$, $Ba(NO_3)_2$	49	*Mg*–		Pb_3O_4, Sb_2S_3	30–32	$KClO_4$, $BaCrO_4$	16, 51, 52
$KClO_4$, AlF_3	15	BaO_2, acaroid resin	18, 19	$K_2Cr_2O_7$	57		
Nitrates, fluorides	37–40	BaO_2, calcium resinate	13	KNO_3	79	*Zr*–	
		$NaNO_3$, $Sr(NO_3)_2$, binders	41, 43–45			MoO_3	24, 26
B–		$LiNO_3$	41	*Ta*–		Fe_2O_3, SiO_2	16
Bi_2O_3	74	$KClO_3$, fluorides	56	PbO, Pb_3O_4	35		
PbO	36, 62	$KClO_4$, dopants	48	$PbCrO_4$	60	*Zn*–	
Pb_3O_4, Cr_2O_3	61, 62	PTFE	75	$KClO_4$	80	$KClO_4$,	
KNO_3	20, 61					hexachlorobenzene	11
Si, KNO_3	18	*Mn*–		*Ti*–		TNT,	
MoO_3	25	$KClO_4$, $BaCrO_4$	76	MoO_3	24	hexachloroethane	82
$K_2Cr_2O_7$, $Na_2Cr_2O_7$	57, 58			TiN, BaO_2	81	*Miscellaneous*	
Si, $K_2Cr_2O_7$	57, 59	*Mo*–		$NaNO_3$, $Sr(NO_3)_2$, binders	43, 44, 46	C, S, KNO_3	14, 66, 83
		BaO_2	77	$KClO_4$, $KClO_3$	54, 55	ZnO, $CaSi_3$,	
				$KClO_4$, $BaCrO_4$	50	hexachloroethane	9
Fe–		*Sb*–				$KClO_3$, lactose, dyes	8
MoO_3	24	$KMnO_4$	16, 34	*V*–		$Ba(ClO_3)_2$, $KClO_4$,	
Fe/Si–Pb_3O_4	28			MoO_3	24	acaroid resin	82
						Silumin, hexachloro-	
						ethane	84

for the pyrotechnic mixture, the components and various subsidiary mixtures. This approach was to form an important part of nearly all subsequent investigations. Of the complementary techniques X-ray diffraction has been the one of paramount importance in the identification of solid reaction intermediates and final products. The samples may be obtained either by interrupting the thermal analysis experiment or separately under conditions determined by those experiments. For the so-called "gassy" pyrotechnics the analysis of the evolved gases provides a parallel to the X-ray diffraction studies of solids but one which as yet has not been widely exploited.

Thermal analysis has been used to investigate the factors which influence the ignition of pyrotechnics. Mention has been made of instrumental parameters but it is the effect of additives which has generated the most interest. Natural products, synthetic polymers and resins form one group of additives which are used to improve the physical characteristics of pyrotechnic mixtures. Thermal analysis has proved to be a successful means of investigating the role of these materials which often play an integral part in the chemistry of the pyrotechnic reaction.

A range of pyrotechnics has been selected for discussion to illustrate various applications of thermal analysis: for the most part concern has been with those publications where DTA and DSC have played a significant part in the experimentation.

3.1. Organic-based pyrotechnics

The pyrotechnics considered in this section are examples of smoke compositions. This is an important category but there have been fewer thermal analysis publications than for delays. The reactions are complicated by the presence of organic materials whereas most of the delays which have been studied are entirely inorganic. Three publications provide an admirable illustration of the application of thermal analysis. In one, Gordon and Campbell [11] described the use of their purpose-built apparatus to investigate pyrotechnic mixtures of zinc, $KClO_4$ and hexachlorobenzene. The DTA curve showed that the mixture ignited and underwent a highly exothermic combustion immediately following the onset of the endotherm of vaporization of hexachlorobenzene at 320 °C. A study of the DTA curves for the binary mixtures of the components led the researchers to conclude that the three reactions

$$3Zn + C_6Cl_6 = 3ZnCl_2 + 6C$$

$$4C + KClO_4 = KCl + 4CO$$

$$4Zn + KClO_4 = KCl + 4ZnO$$

were principally responsible for the ignition and combustion.

Jarvis [9] studied the reactions occurring in pyrotechnic mixtures of ZnO, calcium silicide (formulated as $CaSi_3$) and hexachloroethane. As with the previous pyrotechnic this mixture is used to produce a white smoke which is considered to have the empirical formula $2ZnO \cdot ZnCl_2$. Commercial DTA equipment was used, the components being added separately to quartz crucibles. This technique was used to obtain representative samples (see Section 2.1) but had the added effect of improving the DTA base line. The crucibles were sealed to prevent the loss of hexachloroethane before the onset of reaction. The thermal analysis curve showed an endotherm at 266 ° C which was attributed to the vaporization of hexachloroethane. This was followed by four well-defined exotherms which were identified from a study of the pyrolysis of hexachloroethane and its reactions with ZnO and $CaSi_3$. The first exotherm was attributed to three reactions:

$$CaSi_3 + 3C_2Cl_6 = CaCl_2 + 2CCl_4 + 2C_2Cl_4 + 3Si$$

$$6ZnO + 2CCl_4 = 2(2ZnO \cdot ZnCl_2) + 2COCl_2$$

$$6ZnO + 2COCl_2 = 2(2ZnO \cdot ZnCl_2) + 2CO_2$$

The explanation for the lack of structure of the DTA peak was the rapidity with which the second and third reactions proceeded. The three remaining exotherms were identified with the reactions

$$3CaSi_3 + 3C_2Cl_4 = 3CaCl_2 + C_6Cl_6 + 9Si$$

$$2ZnO \cdot ZnCl_2 + C_2Cl_4 = 3ZnCl_2 + 2CO$$

$$3CaSi_3 + C_6Cl_6 = 3CaCl_2 + 6C + 9Si$$

However, a distinction was made between these reactions which are largely confined to the thermal analysis experiment and the initial reaction sequence which is responsible for the pyrotechnic combustion and smoke production.

The third publication is that by Scanes [8] who investigated mixtures of $KClO_3$ and lactose. This mixture is used to produce a smoke by vaporizing an organic dye. This mechanism is quite different from that involved in the previous mixtures. The work exemplifies the use of thermogravimetry and evolved-gas analysis by means of mass spectrometry to complement the DTA studies. The DTA and evolved-gas analysis curves were recorded for 50% * $KClO_3$–50%lactose diluted with alumina and heated in helium. An endotherm at 138 ° C was attributed to the removal of water of crystallization. This was followed by two exotherms at 200 ° C and 340 ° C respectively. The first coincided with the fusion of the lactose and arose from its oxidation by $KClO_3$:

$$8KClO_3 + C_{12}H_{22}O_{11} = 8KCl + 12CO_2 + 11H_2O$$

There was also some dehydration of the excess of lactose leading to carbonaceous residues which reacted with the remaining $KClO_3$ as it melted to produce the second exotherm. With the sample in air and without the diluent a violent ignition was observed.

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* % = weight of component × 100/weight of mixture, except where otherwise specified.

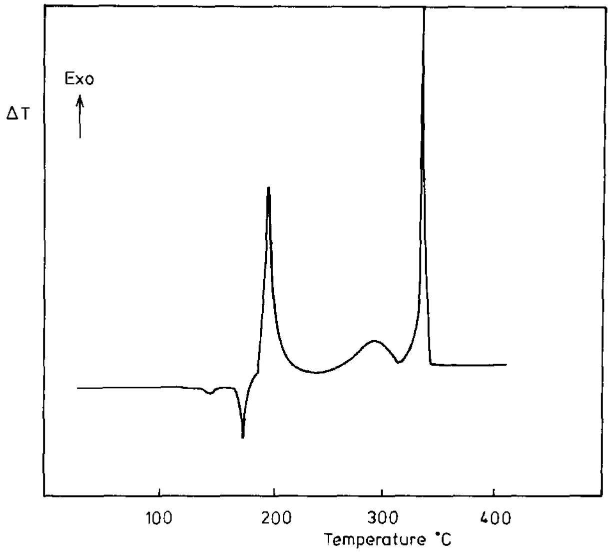

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Fig. 3. DTA curve for a red smoke composition diluted with alumina (1 : 1); total sample mass, 92 mg; heating rate, 4 ° C min^{-1}. Reproduced from F.S. Scanes, Combust. Flame, 23 (1974) 363.

The design of vaporizing pyrotechnics has been considered by Krien [23] who investigated the thermochemistry of a range of dyes with a view to quantifying the energetics of smoke production. This work represents an extension of the earlier study of the interaction of methylaminoanthraquinone with a mixture of $KClO_3$ and lactose. The DTA curve is shown in Fig. 3. The three peaks from the $KClO_3$–lactose reaction are clearly visible. In addition, there is an endotherm at 172 ° C owing to fusion of the dye and an exotherm at 294 ° C owing to partial oxidation of the dye which vaporizes at this temperature. The use of an excess of fuel increases the evolution of gas and lowers the burning temperature compared with the stoichiometric composition. In this way the design objective of rapid removal of the dye without appreciable decomposition can be achieved.

3.2. Pyrotechnics containing molybdenum trioxide

Kirshenbaum and Beardell [24] investigated binary mixtures of MoO_3 and titanium, zirconium, vanadium and iron using simultaneous DTA–thermogravimetry and X-ray diffraction studies. The thermal analysis curves showed a number of exotherms indicating multistage reactions in which MoO_3 was reduced first to MoO_2 and then to elemental molybdenum. The temperature

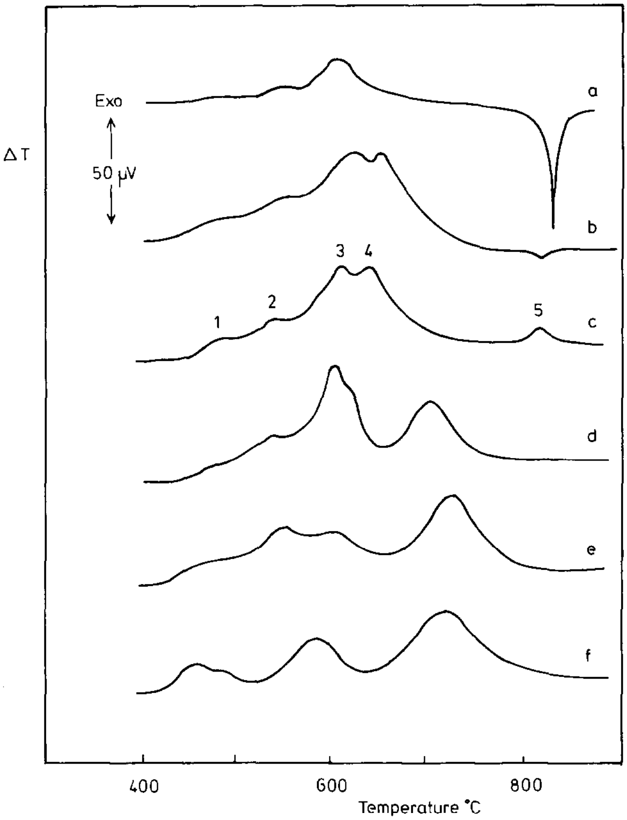

Fig. 4. DTA curves for B–MoO_3 compositions containing the following percentages of boron (sample mass, 50 mg; heating rate, 10 °C min^{-1}): curve a, 2%, curve b, 4%; curve c, 7%; curve d, 13%; curve e, 25%; and curve f, 50%. Reproduced from E.L. Charsley and M.R. Ottaway, in J. Wood, O. Lindqvist and N.G. Vannerberg (Eds.), Proc. 8th Int. Symp. on Reactivity of Solids, 1977, pp. 737–741.

at which reaction became apparent was 465 ± 35 °C and independent of the metal. For zirconium the two stages are

$$Zr + 2MoO_3 = ZrO_2 + 2MoO_2$$

$$Zr + MoO_2 = ZrO_2 + Mo$$

Mixtures of MoO_3 with vanadium and iron produced poorly defined exotherms and were unable to self-sustain the reaction. More recently, Charsley and Ottaway [25] broadened the scope of the investigation to the non-metal boron. The DTA curves are shown in Fig. 4. The reaction scheme is in Table 2. Although it incorporates the formation of Mo_4O_{11}, the pattern of successive reduction of MoO_3 is essentially the same as that proposed with the metals.

The work on the MoO_3–Zr system was extended to investigate the reaction kinetics [26]. The DTA data were examined using a number of

TABLE 2

Reaction scheme for boron-molybdenum trioxide

Exotherm	Reaction
1 and 2	$2B+3MoO_3=B_2O_3+3MoO_2$
3	$2B+12MoO_3=B_2O_3+3Mo_4O_{11}$
4	$2B+Mo_4O_{11}=B_2O_3+4MoO_2$
5	$4B+3MoO_2=2B_2O_3+3Mo$

approaches from which the researchers concluded that the Freeman and Carroll equation [27] gave the most consistent results. The analysis indicated an activation energy of 272 kJ mol^{-1} for both reaction stages. An ingenious approach was adopted to resolve the two overlapping DTA peaks: the first peak was obtained by subtracting the separately recorded peak for the MoO_2–Zr reaction.

3.3. Pyrotechnics containing lead oxides

Pyrotechnics containing lead oxides were among the earliest delays studied by thermal analysis. Mixtures of both silicon and FeSi (92% Si) with red lead (Pb_3O_4) figure prominently in a remarkably detailed study of pyrotechnics by Nakahara during the period 1959–1961. The concern here is with the results of the thermal analysis studies [28] which formed only a small part of the total experimental effort. DTA and thermogravimetry were used to investigate mixtures of FeSi with Pb_3O_4 and of antimony with $KMnO_4$ together with their components. For Pb_3O_4, the thermogravimetric curve showed a 2.5% mass loss which was attributed to a one-stage decomposition, $Pb_3O_4 = 3PbO + 0.5O_2$. This was confirmed by Sulacsik [29]: the DTA and derivative thermogravimetric curves showed a peak temperature of 630 °C. The relationship between this decomposition and the pyrotechnic reaction is not entirely straightforward. The DTA curves for mixtures of silicon and Pb_3O_4 in both air and nitrogen show a number of overlapping exotherms [30,31]. In air a sharp exotherm at 650 °C was observed for some mixtures. This was indicative of ignition. One feature common to all the mixtures studied was an exotherm at 550–600 °C. This was consistent with the decomposition of the oxidant and the simultaneous formation of SiO_2. Clarification of the mechanism was provided by Moghaddam and Rees [32] who used the combination of thermal techniques DSC, thermogravimetry and hot-stage microscopy, complemented by X-ray diffraction. Figure 5 shows the curves obtained by DSC for the mixtures Si–Pb_3O_4 and Si–PbO in nitrogen. It is clear that a common reaction pattern exists with both oxidants. Traces of SiO_2 and lead in the intermediate products were identified by X-ray diffraction: the researchers concluded that the lower tempera-

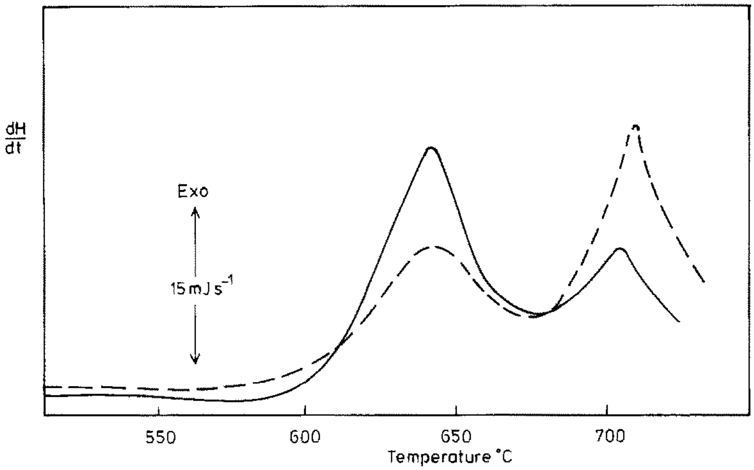

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Fig. 5. DSC curves for PbO–Si and Pb_3O_4–Si containing 20% Si: — — —, PbO–Si; ———, Pb_3O_4–Si. Reproduced from A.Z. Moghaddam and G.J. Rees, Fuel, 60 (1981) 629.

ture exotherm arose from a surface reaction between silicon and PbO to form silica whilst subsequent reaction in the bulk phase produced the higher temperature exotherm. The lower temperature exotherm was not reproduced when the intermediate product was reheated. This is consistent with the presence of SiO_2 on the silicon, inhibiting further surface reaction. Confirmation of the mechanism for mixtures initially containing Pb_3O_4 was obtained from separate thermogravimetric experiments. A mass loss occurred at 450–600 °C and was attributable to the decomposition of the oxidant in which the evolved oxygen was removed from the apparatus by the nitrogen. Hot-stage microscopy was used to investigate the phase changes of the oxidants and the ignition characteristics of the mixtures. With this technique, ignition occurred during the second exotherm at a temperature significantly higher than that recorded by Nakahara [25]. A distinction can be drawn between the conditions which exist in the thermal analysis experiment and those in a delay device where the evolved oxygen may be utilized by the fuel. Other researchers [33,34] in their investigations of FeSi (90% Si)–Mn and Sb–$KMnO_4$ have also drawn attention to this dichotomy. Clearly, care is needed when results from thermal analysis are applied to the interpretation of pyrotechnic reactions in sealed systems.

Other pyrotechnic mixtures investigated by thermal analysis include Ta–PbO_2, Ta–Pb_3O_4 and B–PbO. In their study of the tantalum mixtures, Yoganarasimhan et al. [35] have reported the DTA curves for a range of compositions. The curves showed a well-defined exotherm with a peak temperature in the range 564–605 °C regardless of the initial oxidant, whether PbO_2 or Pb_3O_4. Subsidiary experiments on PbO_2 showed that it decomposed to Pb_3O_4 at a temperature lower than that observed for the pyrotechnic reaction. For mixtures initially containing a high proportion of PbO_2 (more than 60%) there was evidence of a small endotherm just before the onset of the exotherm which the researchers attributed to the decomposition of Pb_3O_4. For some mixtures there was a slight broadening of the base of the exotherm and this was attributed to the reaction of Ta_2O_5 with PbO to form tantalates as revealed by IR analysis of the products. The researchers used the reciprocal peak-width at half-height to assess the rate of reaction and concluded that it was greater when Pb_3O_4 was formed in situ than when it was a component of the initial mixture. However, there is some uncertainty in the detailed quantitative interpretation of the thermal analysis experiments: the researchers commented that the apparent exothermicity values derived from the peak areas were anomalous. It seems that the experiments were carried out with the samples in air and tantalum itself gave a well-defined exotherm at 586 ° C. Thus it is not possible to determine unequivocally the extent to which atmospheric oxidation of tantalum occurred with the mixtures.

For mixtures of boron and PbO a detailed interpretation of the reaction mechanism has been proposed by Goodfield and Rees [36]. DSC curves showed two main exotherms which were attributed to the surface and bulk phase reactions between the components, as in the mechanism proposed for the reaction between silicon and PbO. Attention was drawn to the importance of a surface coating of B_2O_3 on the boron in determining the rate of the main PbO–B reaction.

3.4. Pyrotechnics containing nitrates

The thermal analysis of pyrotechnics containing nitrates owes much to the work of Rosina and Pelhan [37,38] as exemplified by their comprehensive study of heat sources containing aluminium: the earlier publication was concerned with $Al\text{–}KNO_3\text{–}NaF$ and $Al\text{–}KNO_3\text{–}CaF_2$ and the latter with $Al\text{–}NaNO_3\text{–}NaF$ and $Al\text{–}NaNO_3\text{–}CaF_2$. This work itself was a continuation of a wide-ranging investigation [39] of binary and ternary mixtures of aluminium with $NaNO_3$, $Ba(NO_3)_2$, NaF, CaF_2 and Na_3AlF_6. The DTA curve for $Al\text{–}NaNO_3\text{–}NaF$ showed two large exotherms: one occurred at 310–450 ° C and did not appear with the same definition in either of the binary mixtures $Al\text{–}NaNO_3$ or Al–NaF, and the other which was the more dominant, occurred at 850–1080 ° C. Similarly, two exotherms were shown by the corresponding ternary mixture containing CaF_2 but the low temperature peak was rather broader, extending over the temperature range 310–600 ° C. For their interpretation of these exotherms the researchers made extensive use of X-ray diffraction for identifying both intermediate and final products. The low temperature peak was attributed to the decomposition of $NaNO_3$ and the attendant oxidation of aluminium. The high temperature peak was associated with the formation of $Na_2O \cdot 11Al_2O_3$, Al_2O_3 and AlN but the reactions were dependent on the presence of atmospheric oxygen: when samples were studied in argon this peak almost entirely disappeared. For the study of Al–KNO_3–NaF and Al–KNO_3–CaF_2 an analogous approach was adopted and a similar pattern of results emerged. These same researchers [40] evaluated the exothermicity of the ternary mixtures from DTA peak areas using substances of known heats of combustion as calibrants. The researchers reported values for the mixtures both in argon and in air. In the latter case values were obtained for two temperature ranges (300–700 °C and 800–1250 °C) which showed that the high temperature reactions provided the main source of heat.

Freeman and Gordon [41] included the DTA curves for the flares Mg–$NaNO_3$ and Mg–$LiNO_3$ in a publication concerned with the application of absolute rate theory: ignition was observed at 550 °C and 457 °C respectively following the fusion of the oxidants at 315 °C ($NaNO_3$) and 268 °C ($LiNO_3$). The ignition of Mg–$NaNO_3$ was also investigated by Bond and Jacobs [42] by means of self-heating studies. Although strictly not DTA, two thermocouples were used in a differential technique: one thermocouple was located in the sample and the other in the bath of molten metal used to heat the sample. The results suggested that the critical stage in ignition was the decomposition of the $NaNO_3$ to $NaNO_2$ with the simultaneous oxidation of the magnesium.

Barton et al. [43–46] have studied the mixtures Mg–$NaNO_3$, Mg–$Sr(NO_3)_2$, Ti–$NaNO_3$ and Ti–$Sr(NO_3)_2$ with the object of assessing the role of binders in pyrotechnic reactions (see also ref. 47). The DTA curves revealed that the addition of binders introduced new exotherms which arose predominantly from the reaction between the binder and oxidant. The effect of the binder in modifying the DTA curve is also reflected in the observed ignition temperatures. Table 3 shows the ignition temperature of mixtures of titanium and $NaNO_3$ with a range of binders. The binary mixture ignited at 772 °C. The effect can be dramatic; the addition of linseed oil reduces the ignition temperature by more than 350 °C.

TABLE 3

Ignition temperatures of Ti–$NaNO_3$–binder [a]

Binder	Ignition temperature (°C)
Poly(vinylacetate)	768
Saytex 102	749
Beeswax	748
Cereclor 65L	712
Carbon black	533
Boiled linseed oil	407

[a] The composition of the mixtures was 48% Ti, 48% $NaNO_3$, 4% binder.

3.5. Pyrotechnics containing perchlorates and chlorates

Pyrotechnics containing $KClO_4$ have been the subject of many thermal analysis studies most of which have been directed towards the ignition characteristics of the mixtures. These studies include part of the early work from Picatinny Arsenal (see Introduction): the investigation of Zn–$KClO_4$–hexachlorobenzene has already been discussed [11].

Freeman et al. [48] used DTA and thermogravimetry to investigate the ignition of mixtures of magnesium and $KClO_4$. The thermal analysis curves were reproduced with a commentary by Freeman and Rudloff [4]. Two salient features emerged from the DTA curves: the need for a sufficiently high heating rate to engender ignition and the susceptibility of the ignition temperature to the presence of small amounts of dopants in the $KClO_4$. A striking example is the decrease in the ignition temperature by more than 100 °C brought about by the presence of only 1 mol% Ag^+.

The effect of AlF_3 on the combustion of aluminium and $KClO_4$ was investigated by Freeman and Anderson [15]. In the presence of AlF_3 the DTA curve showed an ignition peak at 510 °C whereas in its absence an exotherm principally due to the decomposition of $KClO_4$ was observed at 598 °C. The researchers concluded that AlF_3 and $KClO_4$ reacted to give a complex fluoride $AlF_3 \cdot KF$ according to the equation $2AlF_3 + 3KClO_4 = AlF_3 \cdot KF + AlOCl + Cl_2 + 5.5\ O_2 + 2KF$. Ignition was promoted by both the complex fluoride itself destroying the protective coating of Al_2O_3 on the surface of the aluminium and the gases produced in its formation. An imaginative experiment was devised to confirm the role of these gases. A mixture of $KClO_4$ and AlF_3 was placed in the bottom of a sample tube followed by a layer of Al_2O_3 and finally aluminium powder with a thermocouple in the bottom layer and another in the top layer of aluminium powder. The results are shown in Fig. 6. Curve (a) shows that the ignition of the aluminium powder occurred during an endotherm at 500 °C in curve (b) which corresponded to the formation of the complex. Ignition was not observed in the absence of AlF_3.

Earlier, Hogan et al. [49] investigated the photoflash mixture Al–$KClO_4$–$Ba(NO_3)_2$ and showed that $Ba(NO_3)_2$ catalysed the decomposition of $KClO_4$. The researchers developed the use of DTA and thermogravimetry to analyse these ternary mixtures using the peak area corresponding to the phase transition in $KClO_4$ at 300 °C and the mass loss during the decomposition of the oxidants. Other ternary mixtures which have been investigated include Ti–$KClO_4$–$BaCrO_4$ [50] and W–$KClO_4$–$BaCrO_4$ [51,52]. DTA showed that the predominant reaction was between $KClO_4$ and the fuel. For Ti–$KClO_4$–$BaCrO_4$ a large exotherm was observed at 500 °C. The same exotherm was shown by binary mixtures of titanium and $KClO_4$: the principal effect of the $BaCrO_4$ in the ternary mixture was to reduce the exothermicity. The reaction between tungsten and $KClO_4$ also gave a single

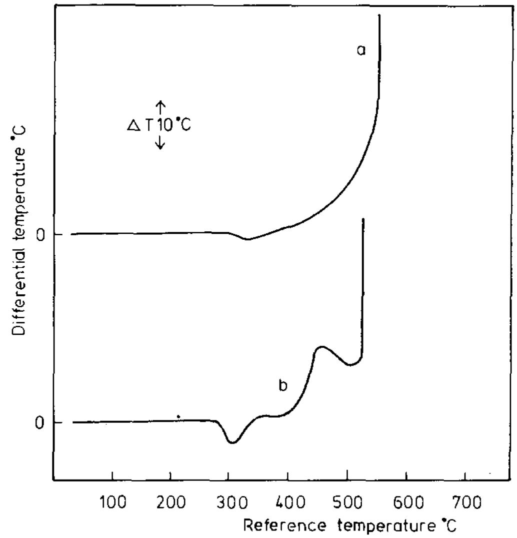

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Fig. 6. DTA curves for Al–$KClO_4$–AlF_3 in a double-layer experiment with the thermocouples located in aluminium (curve a) and in $KClO_4$–AlF_3 (curve b) separated by alumina. Heating rate, 15 °C min^{-1}. Reproduced from E.S. Freeman and D.A. Anderson, Combust. Flame, 10 (1966) 337.

exotherm but here DTA revealed a considerable temperature variation depending on the composition, the particle size of the tungsten and the nature of the atmosphere, whether air or argon. Recently the DTA curves for $LiClO_4$ and its binary mixtures with aluminium, iron, nickel, magnesium and chromium were reported by Kovalenko et al. [53].

Collins [54] has reported the DTA curves for the subhydride $TiH_{0.15}$ with $KClO_4$, $RbClO_4$, KIO_4 and $KClO_3$: all the curves showed ignition of the mixtures at 550 °C. Auger spectroscopy was used to provide detailed information on the surface reaction—an approach which complements the macroscopic scale of thermal analysis studies and promises to broaden our understanding of pyrotechnic reactions considerably. Collins extended the study to $TiH_{0.15}$–$KClO_4$ using DSC together with thermogravimetry and drew attention to a consistency between the results and his conclusions from Auger spectroscopy. The mixture was heated to 450 °C at 20 °C min^{-1} and then held isothermally. The oxidation exotherm which was established during heating returned to the base line but was re-established when the sample was heated further. This indicated that the decelerating rate of oxidation was due to depletion of reactive titanium at the surface and not to completion of the bulk reaction. A slow reaction under isothermal conditions was related to diffusion of oxygen through the TiO_2 lattice. The more rapid reaction was attributed to dissolution of the oxide into the bulk metal and oxidation of the freshly exposed titanium.

The ignition of titanium-based pyrotechnics has been investigated more recently by Erickson et al. [55]. Auger spectroscopy was used to examine isothermally oxidized single crystals of titanium. The researchers concluded that the mechanism leading to ignition under the conditions of a thermal analysis experiment was the growth of a TiO_2 layer adjacent to the gas–solid interface rather than the dissolution of oxygen into the bulk metal. Of particular interest in the context of the present review was the development of a theoretical model for the response of a DTA instrument to a pyrotechnic ignition reaction. This incorporated the kinetic scheme for the growth of TiO_2 but the approach promises a much wider application. Erickson et al. showed that the predicted ignition exotherms were similar to those observed by Collins.

There have been fewer publications on the thermal analysis of pyrotechnics containing chlorates: reference has already been made to the work of Scanes [8] on $KClO_3$–lactose. Earlier, Campbell and Taylor [56] made a study of the effect of fluorides on the reaction between magnesium and $KClO_3$. The use of NaF was of key interest in view of its non-hygroscopicity. Binary mixtures of magnesium and $KClO_3$ do not self-sustain combustion: the DTA and thermogravimetric curves showed that incomplete oxidation of the magnesium accompanied the decomposition of $KClO_3$, beginning just above its melting temperature (365 °C). With the addition of NaF the decomposition temperature of $KClO_3$ was raised to 490 °C and the subsequent exothermic reaction culminated in ignition of the mixtures. A detailed examination of the thermal analysis data together with the results of X-ray diffraction provided the basis for an explanation of the enhanced ignitability. The researchers concluded that in the presence of NaF the evolution of oxygen was inhibited until the temperature was attained at which the self-sustained combustion could be established. The effect of the NaF was to enhance the formation of the thermally more stable $KClO_4$ and to nullify the catalytic effect of magnesium on the decomposition of $KClO_3$. Furthermore, NaF reacted with magnesium to form sodium which in turn reacted with oxygen to trigger the self-sustained combustion.

3.6. Pyrotechnics containing dichromates and chromates

Mixtures of boron and $K_2Cr_2O_7$ were first studied by Howlett and May [57] using DSC. An unusual feature was the choice of dry oxygen as an atmosphere for the experiments. The rather limited temperature range, ambient to 500 °C, was determined by the instrument: the separate components were shown to be chemically inert over this temperature range. More recently, Charsley et al. [58] extended the temperature to 1000 °C using DTA which revealed a high temperature reaction essential to the self-sustained combustion. Under non-ignition conditions both DSC and DTA curves showed the onset of an exothermic reaction just preceding the fusion of the oxidant (at about 398 ° C) which was immediately followed by a rapid exothermic reaction. The importance of the fusion process was illustrated in the DSC experiments by replacing $K_2Cr_2O_7$ with either $Na_2Cr_2O_7$ or a mixture of $K_2Cr_2O_7$ and $Na_2Cr_2O_7$: in both cases the main exothermic reaction occurred at the new fusion temperature. The DTA studies were directed to mixtures containing 4%–7% B. Measurement of the DTA peak areas showed that the exothermicity was significantly reduced when mixtures contained less than 4% B. This is consistent with the stoichiometric amount of boron (3.5%) required by the equation, $2B + 2K_2Cr_2O_7 = B_2O_3 + 2K_2CrO_4 + Cr_2O_3$. The formation of K_2CrO_4 was confirmed by X-ray diffraction.

Mixtures containing more than 4% B showed a second exotherm which was attributed to the reaction of K_2CrO_4 with the excess boron. It was this reaction which was found to play an essential part in the self-sustained combustion and mixtures containing only 4% B, in which this second reaction was absent, did not burn. Under ignition conditions, the DTA curve showed only a single large exotherm starting at 377 ° C with a measured temperature rise ranging from 30 to 300 ° C. It is necessary to distinguish between this exotherm and the lower temperature exotherm recorded under non-ignition conditions: in the DSC experiments the recorded peak almost certainly related to non-ignition conditions. Charsley et al. [59] have used DTA to study the effect of adding silicon to the binary mixtures of boron and $K_2Cr_2O_7$. The curves show that its presence does not influence the first reaction stage but increases the exothermicity of the second. The result is that mixtures prepared from the binary mixture containing only 4% B are able to self-sustain the combustion.

DTA has also been used to investigate the nature of the reaction between tungsten and $K_2Cr_2O_7$ [10]. Under ignition conditions, mixtures containing 20%–90% W ignited at 380–390 ° C to give a single exotherm. A quantitative evaluation of the exothermicity from the area of this ignition peak gave

TABLE 4

Exothermicity of the ignition reaction between tungsten and $K_2Cr_2O_7$

% W	Exothermicity (kJ g^{-1})	
	DTA	Combustion calorimetry
40	1.20 ± 0.06	1.34 ± 0.02
50	1.06 ± 0.07	1.14 ± 0.02
60	0.89 ± 0.07	0.88 ± 0.02
70	0.68 ± 0.06	0.68 ± 0.02
90	0.25 ± 0.01	0.21 ± 0.03

values which, with one exception, were in agreement with those determined by combustion calorimetry (Table 4).These results are consistent with the following equation:

$$W + K_2Cr_2O_7 = K_2WO_4 + Cr_2O_3$$

Under non-ignition conditions, the DTA curves showed similarities to those recorded for the boron mixtures. A large exotherm was observed immediately following the fusion of the oxidant; mixtures containing more than 30% W gave a second exotherm at 730 °C. This second exotherm was ascribed to the reaction $W + WO_3 + 2K_2CrO_4 = 2K_2WO_4 + Cr_2O_3$, and subsidiary experiments showed that a mixture of tungsten, WO_3 and K_2CrO_4 gave a peak of similar appearance. However, unlike the boron system the second exotherm was poorly defined and the ternary mixture of the components did not support combustion.

The use of DTA to investigate pyrotechnic mixtures containing chromates is illustrated by the recent study of Ta–$PbCrO_4$ by Sarawadekar et al. [60]. The work was an extension of earlier studies [35] of Ta–PbO_2 and Ta–Pb_3O_4. A difference of approach was in the preparation of the pyrotechnic mixtures by co-precipitation where a solution of $Pb(NO_3)_2$ was added to a suspension of tantalum powder in a solution of K_2CrO_4. Ill-defined exotherms were obtained starting in the temperature range 568–583 °C which is significantly lower than the temperature at which $PbCrO_4$ itself decomposes. The researchers suggested that the exotherms originated from the reaction

$$10PbCrO_4 + 6Ta = 3Ta_2O_5 + 10PbO + 5Cr_2O_3$$

An atmosphere of nitrogen was used in the experiments and for mixtures containing 49% tantalum or more there was evidence of a higher temperature exotherm overlapping the first, owing to the formation of TaN. Experiments were also carried out with the samples in air, and these gave quite different results. Well-defined single exotherms reminiscent of those obtained with PbO_2 and Pb_3O_4 were observed, but with the peak temperatures higher, in the range 643–657 °C. These studies provide a clear indication of the difficulties inherent in the interpretation of data obtained from experiments involving reactive atmospheres. Goodfield and Rees [36] have drawn attention to some of the differences to be expected in the thermal analysis of co-precipitated pyrotechnics compared with those prepared by the more conventional methods.

4. DISCUSSION

Publications concerned with reaction mechanisms have formed a significant part of the literature on pyrotechnics. However, it should not be inferred that the difficulties inherent in the interpretation of the experimental data have been resolved entirely. In spite of the wide range of analytical techniques that are now employed it has seldom proved possible to identify all the reaction intermediates and products. The chemical equations which have been proposed for pyrotechnic reactions must therefore be regarded with some reservation. Inevitably, the usefulness of X-ray diffraction is severely restricted for those pyrotechnics where the solid products are formed as glasses. Combustion calorimetry has been used to investigate the overall stoichiometry of pyrotechnic reactions under conditions approaching those likely to exist in a practical device. The assignment of peaks recorded by DTA and DSC has been supported by thermogravimetry which has been used extensively in the study of pyrotechnics. Patterns of behaviour have emerged from the thermal analysis studies. Perhaps the most obvious is the successive reduction of the oxidant as exemplified by the pyrotechnic reactions involving MoO_3. Another is the sequence of surface reaction followed by bulk phase reaction which has been reported for a small number of pyrotechnics. Many reactions proceed at a temperature significantly lower than that at which the pure oxidant decomposes. For some pyrotechnics the DTA curves indicate that it is the fusion or vaporization of a component which promotes the onset of propagative combustion. Reference has already been made to the differences which exist between the conditions in a DTA experiment and those in a delay device. Removal of the oxygen evolved during an experiment by the use of an inert gas may inhibit ignition and give rise to diffuse exotherms. In such circumstances an atmosphere containing oxygen may model the situation of a practical delay but experiments using an inert atmosphere are invaluable to enable a clear distinction to be made between atmospheric oxidation and the pyrotechnic reaction.

DTA and DSC have not found extensive application in the measurement of exothermicity despite the means they provide for estimating the contribution of the individual reaction stages. In this context the work of Rosina and Pelhan [40] makes a major contribution with their results for pyrotechnics containing nitrates. The values obtained by Charsley et al. [10] (Table 4) refer to ignition conditions. The agreement observed between these values and those from combustion calorimetry is rather surprising since the equipment is not expected to follow the rapid rate of temperature rise of the sample. It may be that in this instance it is the gasless nature of the $W-K_2Cr_2O_7$ pyrotechnic which is responsible for the success of the technique. For the pyrotechnic $B-K_2Cr_2O_7$ there is a discrepancy between the total exothermicity obtained under ignition conditions and the values derived from the individual reaction stages [58]. More recently, Whelan et al. [61,62] have used DSC to measure the exothermicity of mixtures of boron as part of a study of reaction kinetics. There are several examples in the literature [30,35,60] where area measurements have been used to estimate relative exothermicities without the need for an experimental calibration. The pyrotechnic $B-KNO_3$ has been suggested as a secondary energy standard [63]. The National Bureau of Standards has available three compositions containing zirconium and $BaCrO_4$ for use as heat source standards but they are less suitable as DTA standards. Failure to remove atmospheric oxygen from the sample-holder assembly will lead to appreciable oxidation of the zirconium before the onset of the pyrotechnic reaction.

Speculation has arisen over the possible relationship between DTA peak shape and the burning characteristics of pyrotechnics. It would seem that diffuse peaks are often associated with poor propagative combustion. However, the evidence for a correlation between the peak shape and ignition performance is conflicting [64,65]. The use of DTA and DSC as a source of information on reaction kinetics has been limited: the study of $Zr-MoO_3$ by means of DTA has already been discussed [26]. Kirshenbaum [66] used a similar technique with black powder and was able to correlate changes in activation energy with the nature of the charcoal. There is disagreement between this researcher's conclusion that all three components (sulphur, carbon and KNO_3) take part in the pre-ignition reaction and the results obtained earlier by Campbell and Weingarten [14] which showed that only sulphur and KNO_3 were involved. The discrepancy may arise from the different experimental conditions, i.e the use of considerably smaller samples and an atmosphere of argon compared with air in the earlier study. More recently, DTA curves for binary mixtures of charcoal with both KNO_3 and KNO_2 have been published as part of a comprehensive study of the oxidation of charcoal [67].

Two recent publications [61,62] on mixtures of boron have brought about a renewal of interest in the use of thermal analysis to investigate the kinetics of pyrotechnic reactions. The mixtures $B-KNO_3$, $B-Pb_3O_4$, B–PbO and $B-Pb_3O_4-Cr_2O_3$ were studied by DSC: the kinetic parameters were obtained from the dependence of peak temperatures on heating rate [68,69]. For $B-KNO_3$, two overlapping peaks were obtained and the analysis was restricted to the high temperature main peak. A more straightforward approach was possible with $B-Pb_3O_4$ and $B-Pb_3O_4-Cr_2O_3$ which showed only a single exotherm. The researchers drew attention to the similarity which exists between the results for $B-Pb_3O_4$ and B–PbO with the implication that there is a common reaction step. Table 5 summarizes the thermochemical and kinetic results for the four pyrotechnic mixtures. Kinetic investigations even of simple systems are often contentious and the applicability of thermal analysis results to the propagation process is not self-evident since they are obtained from non-ignition studies at relatively low temperatures.

Thermal analysis has played a significant part in ignition studies of pyrotechnics. The effect of dopants and binders on ignition temperature has already been discussed whilst the investigation of Altham et al. [70] further illustrates this area of study. Ignition temperatures are dependent on the experimental conditions under which they are measured. Differences here

TABLE 5

Kinetic parameters for pyrotechnic mixtures of boron

	$B-KNO_3$	$B-Pb_3O_4$	$B-Pb_3O_4-Cr_2O_3$	B-PbO
Exothermicity ($J\ g^{-1}$)	3315 [b]	846 [c]	730	
Activation energy ($kJ\ mol^{-1}$)	286	434 [c]	391	435
$\log_{10} A$ [a] (s^{-1})	16.3	29.7 [c]	26.2	30.3

[a] A is the pre-exponential factor.

[b] Total exothermicity from the area under the two peaks.

[c] Mean result from isothermal and dynamic experiments.

can often explain the apparent discrepancies between the values reported in the literature. If ignition temperatures are to be used on a comparative basis, it is essential that the experimental conditions be precisely defined. DTA has been used to rank solid fuels (coals, peats and lignites) according to ignition temperature by the addition of $NaNO_2$ [71]. Charsley et al. [18] have investigated the effect on ignition temperature of sample mass and heating rate (see also ref. 19). For $Mg-BaO_2$-acaroid resin, the ignition temperature is decreased by over 200 ° C when the sample mass is changed from 50 to 70 mg: a result of obvious implication in the assessment of performance. The effect on confining the sample to a constant volume [16] has already been mentioned. In some individual cases it has proved to be quite dramatic, on the one hand, engendering ignition with $Zr-Fe_2O_3-SiO_2$ and on the other, precluding ignition with $Sb-KMnO_4$. The rapid nature of DTA and DSC experiments together with the need for only small samples means that quality assurance and the evaluation of chemical reactivity may be carried out on a regular basis. The use of thermal analysis for testing munition components has been described by Rochat and Imhof [72]. Thermal analysis provides an initial assessment on which large-scale experiments may be designed to measure burning velocity and light output which are fundamental to the application of pyrotechnics.

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