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DIFFERENTIAL THERMAL ANALYSIS AND TEMPERATURE PROFILE ANALYSIS OF PYROTECHNIC DELAY SYSTEMS: SLOW BURNING MIXTURES OF BORON AND POTASSIUM DICHROMATE

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ABSTRACT

The slow burning pyrotechnic reaction between boron and potassium dichromate has been studied by differential thermal analysis and temperature profile analysis. The latter technique in which the combustion process is studied directly, shows the presence of two reaction stages and validates the results from differential thermal analysis obtained under non-ignition conditions. In the first stage potassium dichromate is reduced by boron to form potassium chromate. Differential thermal analysis shows that the reaction takes place below the melting temperature of potassium dichromate and becomes much more rapid above this temperature. The second stage which occurs in the region of 1000 K involves the reaction of potassium chromate with more boron. The first stage acts as a trigger for the second and it is this latter stage which propagates the combustion.

INTRODUCTION

Pyrotechnic delay systems consist of finely divided mixtures of a combustible fuel and an oxidant. They burn at a constant rate even in the absence of air and are used as self-contained timing or delay devices. The burning rate is determined by a variety of factors including the nature of the fuel and oxidant and their relative proportions in the mixture. Metallic and non-metallic elements or organic substances are commonly used as fuels with inorganic oxides and oxysalts as oxidants*.

The self-propagating combustion process can involve a rate of temperature rise as high as 10^6 K min^{-1} which is completely outside the heating rates employed in conventional thermal analysis. Although a number of papers have been published in

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* A comprehensive account of pyrotechnics is given by H. Ellern in *Military and Civilian Pyrotechnics*, Chemical Publishing Co. Inc., New York, 1968.

which reactions of pyrotechnic mixtures have been studied by thermal analysis, it has not been shown that the reactions observed are those which occur in the self-propagating process itself. This paper describes a collaborative study in which the technique of temperature profile analysis has been combined with differential thermal analysis (DTA) to investigate the slow burning boron–potassium dichromate mixtures containing 5–7% boron*. These mixtures are typical of the so-called gasless systems where the combustion takes place with little or no loss of weight. This makes DTA particularly well suited to their study.

With pyrotechnic mixtures DTA experiments can be carried out under either ignition or non-ignition conditions. A proper interpretation of the results can only be made in the context of the conditions used. The conditions required to achieve either ignition or non-ignition will depend on the reactivity of the pyrotechnic mixture, the design of the DTA head, the sample weight and the heating rate. Under ignition conditions, where the samples burn, a single large exothermic peak is observed often involving a measured temperature rise of several hundred degrees. Under non-ignition conditions several smaller peaks are observed, and although more information can be obtained its relevance to the self-propagating combustion process is not self-evident since the experiments do not involve ignition. In both techniques the heating rates (5–20 K min^{-1}) are several orders of magnitude less than in the self-propagating combustion process.

In temperature profile analysis, it is the self-propagating process itself which is under study. The temperature profile across the burning zone is measured directly. Analysis of the measurements leads to information which can be represented in a form similar to a DTA curve. Temperature profile analysis is an extension of the method originally described by Hill and his co-workers in 1950–1954[1, 2], and at present is restricted to gasless systems.

Boron–potassium dichromate delay mixtures (containing 4 and 10% boron) have been studied previously by Howlett and May[3] using a differential scanning calorimeter in the temperature range ambient – 773 K with the object of correlating the onset of reaction with the fusion of the oxidant. It was hoped that the present approach of combining DTA with temperature profile analysis would lead to a more detailed understanding of the pyrotechnic reaction between boron and potassium dichromate and provide the basis for future work on other pyrotechnic systems.

EXPERIMENTAL

Materials

Amorphous boron 90–92% (Trona brand, American Potash and Chemical Corp.) was used for preparing the mixtures. This type of boron is normally used in pyrotechnics because high purity amorphous boron is not readily available and the crystalline varieties are less reactive. Experiments carried out with a small amount of

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* Throughout this paper % = weight of component × 100/weight of mixture.

99% pure amorphous boron gave results which did not differ significantly from those reported here. The Trona boron had a nominal particle size of 0.8 μm using the Fisher Sub-sieve Sizer. The potassium dichromate (Analar grade) was obtained from BDH and was ball-milled to a particle size of 4.6 μm (Fisher Sub-sieve Sizer).

Mixtures were prepared by sieving the components through a 200-mesh sieve and then brush mixing the weighed components once through a 100-mesh sieve and twice through a 200-mesh sieve.

Temperature profile analysis

Measurements were made with platinum–platinum/10% rhodium thermocouples, 100 μm in diameter, embedded in the pyrotechnic mixture. The junctions were made by welding the wires with a miniature gas–oxygen flame and were thoroughly annealed and tested for mechanical strength before use. The pyrotechnic mixture was compacted into an open train about 10 cm long, 1 cm high and 1 cm wide on an asbestos board. The thermocouple was stretched across the train with the junction at the mid-point of the mixture. A reference thermocouple was immersed in an ice-bath. The mixture was ignited at one end of the train with a bunsen flame and the thermocouple signal was captured by a transient recorder (Data Laboratories, Model DL 905) and stored as 1024 digital points (8 bits) at equally spaced time intervals. In most experiments the signal was recorded over a total time of either 0.5 or one s. Readings over a longer time base showed that the final signal at ambient temperature was the same as the initial signal, indicating that the thermocouple junction had remained unaffected by the passage of the combustion wave. The stored signal was examined visually on an oscilloscope and recorded in digital form on a punched tape (Facit tape punch, Model 4070).

The basis of the analysis is eqn (1) which is assumed to describe the local heat balance over any cross-section of the pyrotechnic mixture normal to the axis of propagation.

$$\frac{k}{v^2} T_{tt} - \sigma c T_t + \sigma w - h(T - T_a) = 0 \qquad (1)$$

where T is the temperature and the subscript t indicates differentiation with respect to time. T_a is the ambient temperature, v, k, σ and c are the burning velocity, thermal conductivity, density and specific heat capacity, respectively, and are assumed constants for a given pyrotechnic mixture. The term $h(T - T_a)$ allows for lateral heat loss where h is the effective lateral heat loss coefficient which is assumed to be constant. The mechanism of heat transfer is not specified and the best value of h is determined in the analysis. w is the rate of evolution of heat (power) due to chemical and physical changes within the pyrotechnic mixture and is the primary concern of the analysis.

The basic equation may be simplified by working in terms of the temperature excess above the ambient value $U = T - T_a$. Thus dividing eqn (1) by σc we obtain

$$Dv^{-2}U_{tt} - U_t + \frac{w}{c} - \frac{U}{t_{th}} = 0 \qquad (2)$$

where $t_{th} = \sigma c/h$ is the thermal relaxation time in the presence of only lateral losses and D is the thermal diffusivity ($k/\sigma c$). This equation may be re-arranged to give

$$G \equiv \frac{w}{c} = U t_{th}^{-1} + U_t - t^* U_{tt} \tag{3}$$

where t^* represents the time Dv^{-2}. The quantity G which is a measure of the required power is found from eqn (3) and the recorded temperature history. The value U is obtained directly from the temperature profile but the accurate determination of U_t and U_{tt} particularly the latter is difficult. Their calculation is based on a convolution procedure[4]. The times t_{th} and t^* are evaluated from the initial and final portions of the profile where there is no reaction. In these portions $w = 0$ and so eqn (3) gives

$$U t_{th}^{-1} + U_t - t^* U_{tt} = 0 \tag{4}$$

which is a second order differential equation with solutions of the form $U = Ae^{\alpha t}$ where A and α are constants. A is arbitrary but α must meet the condition $t^* t_{th} \alpha^2 - t_{th} \alpha - 1 = 0$ from which we conclude that $t^{*-1} = \alpha_1 + \alpha_2$ and $-1/t_{th} t^* = \alpha_1 \alpha_2$. Values of α_1 and α_2 are derived from plots of ln U against time for the initial and final portions of the profile. A fuller account of both the experimental technique and the numerical processing of the results will be published elsewhere. It should be emphasised that temperature profile analysis is in its early stages of development. The raw experimental data require a considerable amount of numerical processing, and at present, there is no unequivocal procedure for smoothing the data.

Differential thermal analysis

DTA studies were carried out using high temperature DTA equipment (Stanton Redcroft, Models Standata 6-25 and DTA 673). These models have platinum–platinum/13% rhodium thermocouples in a single stem ceramic head and nichrome wire furnaces, and operate over the temperature range ambient to 1300 K. The experiments were carried out in dimpled platinum/rhodium crucibles in a downward flow of high purity argon (100 cm^3 min^{-1}) to avoid aerial oxidation of the boron. Calcined aluminium oxide was used as the reference material.

Ignition experiments were carried out at a heating rate of 20 K min^{-1} using samples weighing 30–50 mg. Measurements under non-ignition conditions were made by reducing the heating rate to 5 K min^{-1} and using samples weighing 20 mg.

Quantitative measurements were made using a recorder (Leeds and Northrup, Model W) fitted with an integrator (Disc, Model 224). For ignition experiments the differential thermocouple output was fed directly into the recorder, by-passing the DTA amplifier, thus reducing the response time to the recording system. There was a tendency for the reaction products to be ejected from the crucible leading to spurious results unless lids were fitted and the minimum weights were used. Even so, the movement of the enclosed sample made it difficult to obtain results of high precision. Under non-ignition conditions the peak areas were measured using the baseline construction described by Cunningham and Wilburn[5]. The peaks were often very broad and this may lead to a systematic error in the results. The DTA head was calibrated by recording the curves for fusions and crystalline transitions of known enthalpy change. The technique will be dealt with in detail elsewhere.

Combustion calorimetry

Measurements were made with an adiabatic combustion calorimeter (Baird and Tatlock) which was calibrated with benzoic acid (BDH, thermochemical grade). The pyrotechnic mixtures were compacted and burnt in a silica crucible in an atmosphere of argon. They were ignited by passing an electric current through a fine platinum wire in contact with the mixture.

X-ray analysis

Powder photographs were obtained using a Debye–Scherrer camera (Enraf-Nonius) with Cr-K_α radiation.

RESULTS

Temperature profile analysis

The temperature profiles showed considerable variations even when recorded for the same mixture. These variations were inevitable because of the irregular nature of the burning process. With solids, it is not possible to reproduce precisely the immediate environment of the thermocouple junction in the mixture. All the temperature profiles showed a rapid temperature rise to the maximum value which was

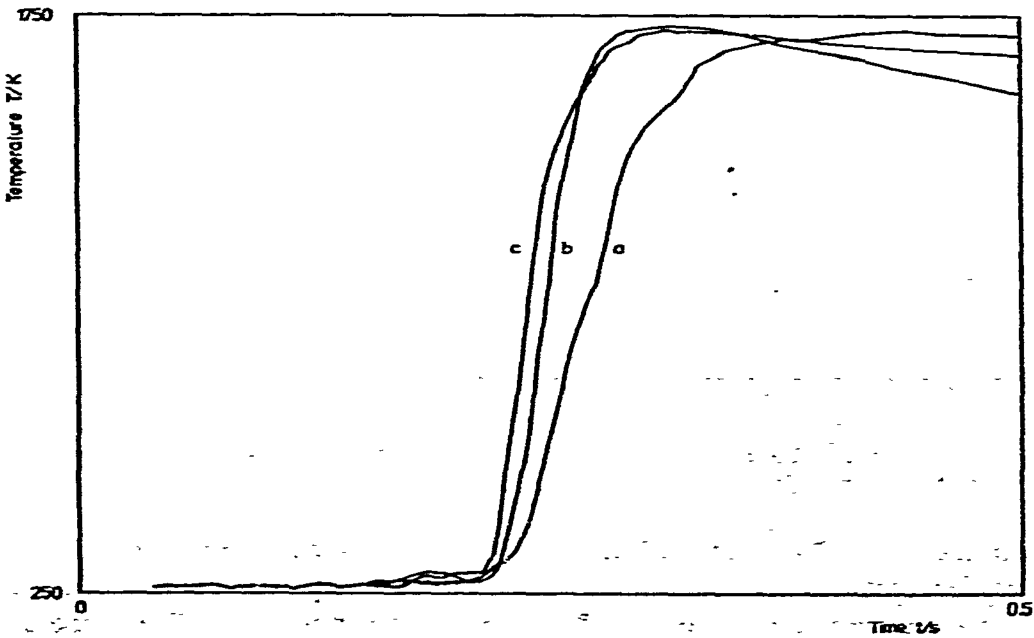

Fig. 1. Temperature profiles for mixtures containing (a) 5%; (b) 6%; and (c) 7% boron.

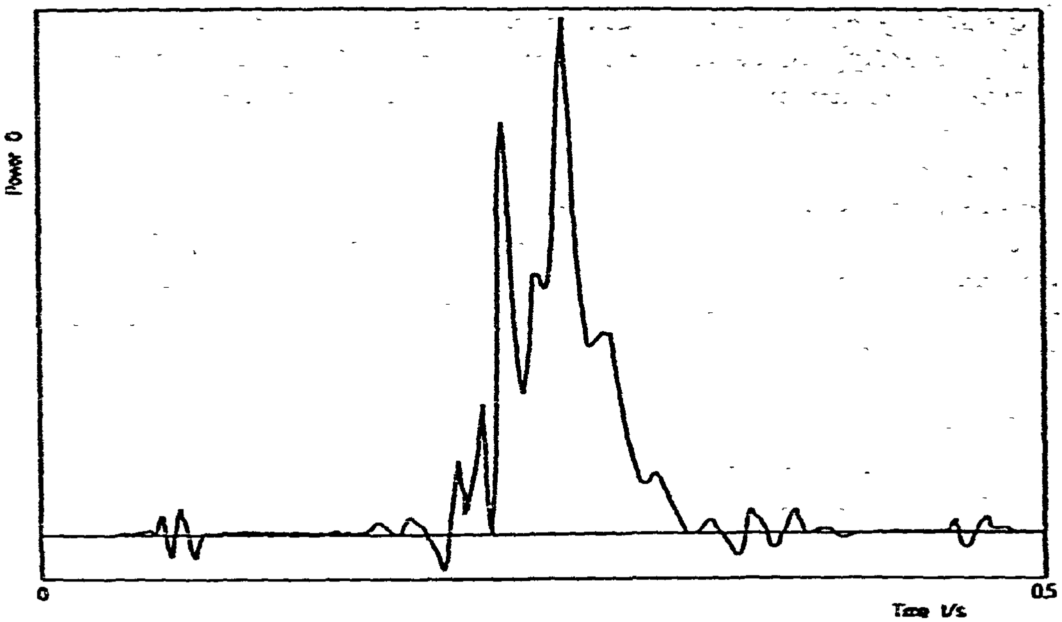

Fig. 2. Power function for the 5% boron mixture.

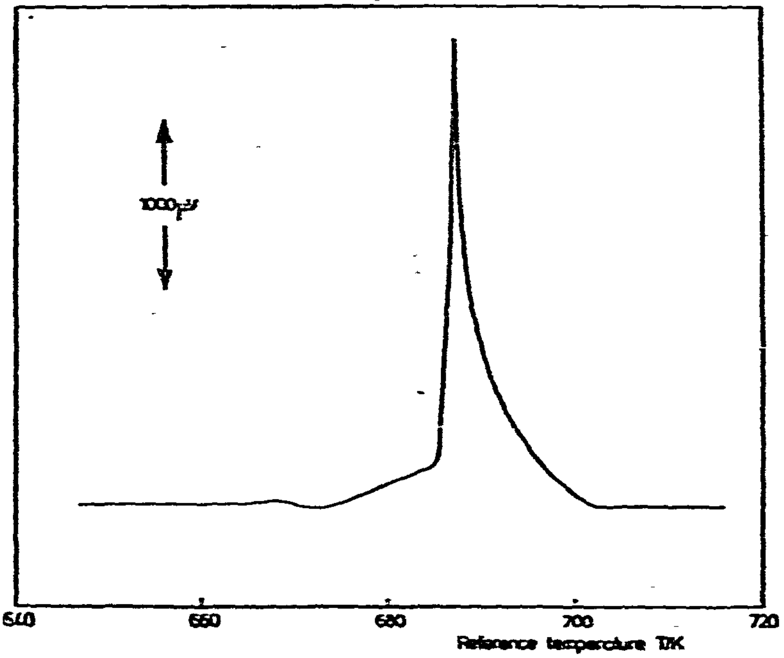

Fig. 3. DTA curve for a 5% boron mixture recorded under ignition conditions. Sample weight, 30 mg; heating rate, 20 K min^{-1}; atmosphere of argon, 100 cm^3 min^{-1}.

commonly in the range 1700–1750 K. The effect of increasing the proportion of boron seemed to be an increase in the initial rate of temperature rise. Examples of temperature profiles for mixtures containing 5, 6 and 7% boron are shown in Fig. 1. The temperature profiles showed that ignition, which was indicated by a significant deviation from

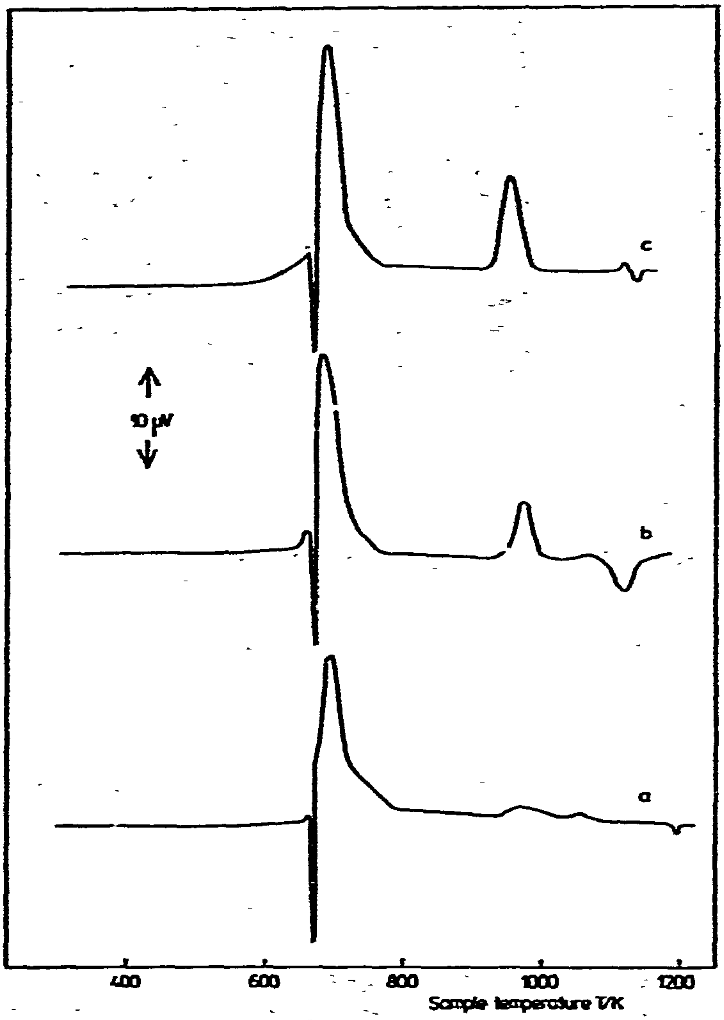

Fig. 4. DTA curves for mixtures containing (a) 5%; (b) 6%; and (c) 7% boron recorded under non-ignition conditions. Sample weights, 20 mg; heating rate, 5 K min^{-1}; atmosphere of argon, 100 cm^3 min^{-1}.

the exponential temperature rise, occurred in the region of the melting temperature of potassium dichromate. Figure 2 shows the form of the power function for the 5% boron mixture obtained by averaging the results from several experiments. This procedure can reduce the effect of poor reproducibility and electrical noise which would otherwise obscure the meaningful features of the power plots. Two exothermic peaks were common to most of the power plots and occurred with the maxima in the temperature ranges 700–1000 K and 1000–1500 K, respectively.

DTA ignition experiments

The DTA curves showed a large exothermic peak with a measured temperature rise of between 50–300 K. The rise in the temperature of the samples themselves was considerably greater. At sufficiently high sensitivity, the start of an exotherm could

TABLE 1

TOTAL REACTION EXOTHERMICITIES

% *Boron*	*Exothermicity (kJ g^{-1})*[a] *Ignition DTA*	*Temperature profile analysis*	*Combustion calorimetry*
5	2.17 ± 0.18	2.18 ± 0.55	2.33 ± 0.02
6	2.46 ± 0.22	2.42 ± 0.61	2.66 ± 0.04
7	2.72 ± 0.18	2.44 ± 0.61	3.10 ± 0.02

[a] The units refer to one gram of mixture.

TABLE 2

EXOTHERMICITIES OF THE FIRST AND SECOND REACTION STAGES MEASURED BY NON-IGNITION DTA

% *Boron*	*Exothermicity (kJ g^{-1})*[a] *First exotherm*	*Second exotherm*	*Total*
5	1.23 ± 0.07	0.21 ± 0.08	1.44 ± 0.11
6	1.19 ± 0.07	0.27 ± 0.02	1.46 ± 0.07
7	1.24 ± 0.09	0.48 ± 0.03	1.72 ± 0.09

[a] The units refer to one gram of mixture.

be observed at about 650 K which is below the melting temperature of pure potassium dichromate (671 K). Superimposed on this exotherm was the endotherm of fusion of potassium dichromate, which was immediately followed by the main exotherm. The temperature of the pre-ignition exotherm was dependent on the experimental conditions. The DTA curves for the 5% boron mixture are shown in Fig. 3.

DTA non-ignition experiments

The non-ignition DTA curves are shown in Fig. 4. They all show an exotherm starting in the region of 650 K and extending to 770 K and the superimposition of the fusion endotherm of potassium dichromate. The maximum of the exotherm was at about 710 K and the peak area was independent of the proportion of boron in the mixture. A second exotherm is observed with an extrapolated onset temperature of about 950 K. For the 5% boron mixture the second exotherm was very poorly defined, but for the 6 and 7% boron mixtures, it was clearly resolved with the size increasing from the 6 to 7% boron content. The peak temperature of the second exotherm was at about 970 K. DTA curves on cooling also show a small peak at about 940 K which corresponds to the solid transition in potassium chromate[6].

Reaction exothermicities

The results from DTA ignition experiments and the values obtained by integrating the temperature profile power plots are shown in Table 1. The specific heat capacity was estimated to be 1.51 J K^{-1} g^{-1} based on differential scanning calorimetry (Perkin-Elmer, Model DSC 1b). It is not possible to obtain an entirely reliable value because of the large temperature range and complex chemistry involved in the combustion process. The same value of the specific heat capacity was used for each of the mixtures and an uncertainty of ± 25% was assigned to it. Also shown in Table 1 are the combustion calorimetric results.

The exothermicities of the first and second exotherms obtained by DTA under non-ignition conditions are shown in Table 2. The errors quoted in the tables take into account the uncertainties in the calibration experiments and the subsidiary data.

DISCUSSION

Temperature profile analysis showed that there are two main exothermic stages in the pyrotechnic reaction between boron and potassium dichromate separated by 300–500 K. This has been achieved by a higher level of instrumental resolution than was possible previously. Under ignition conditions, DTA with its considerably slower response time, was unable to resolve these stages and a single ignition peak was obtained. Both techniques give values for the total exothermicity that agree within the rather large uncertainties. In each case, X-ray analysis showed the presence of potassium chromate and chromic oxide in the products. These results suggest that the reactions in the self-propagating combustion process also occur under DTA ignition conditions. The calorimetric values for the exothermicity shown in Table 1 are in agreement with the DTA and temperature profile analysis results for the 5 and 6% boron mixtures but there is a discrepancy, which is as yet unaccounted for, in the results for the 7% mixture.

DTA under non-ignition conditions showed two well-resolved peaks separated by 200–300 K in accord with the results from temperature profile analysis. The slower rates of heating compared with that in the self-propagating combustion, allowed the reaction stages to be studied in greater detail and the exothermicity to be determined for the individual stages. The values derived from the two peaks are shown in Table 2.

X-ray analysis of the products from the first reaction exotherm showed the presence of potassium chromate which is confirmed by the peak for the solid transition observed in the DTA curve. There was no evidence for the presence of potassium dichromate in the products. Values for the exothermicity of the first reaction stage are shown in Table 3 and include those values already discussed together with the results of subsidiary measurements on mixtures containing less than 5% boron. They show a significant decrease when the proportion of boron is reduced below 4% which is consistent with the stoichiometric amount of boron (3.5%) required by the equation

$$B + K_2Cr_2O_7 = K_2CrO_4 + 0.5\,Cr_2O_3 + 0.5\,B_2O_3$$

TABLE 3

EXOTHERMICITIES OF THE FIRST REACTION STAGE MEASURED BY NON-IGNITION DTA

% Boron	1	2	3	4	5	6	7
Exothermicity ($kJ\ g^{-1}$)[a]	0.25 ± 0.06	0.62 ± 0.06	0.95 ± 0.07	1.21 ± 0.07	1.23 ± 0.07	1.19 ± 0.07	1.24 ± 0.09

[a] The units refer to one gram of mixture.

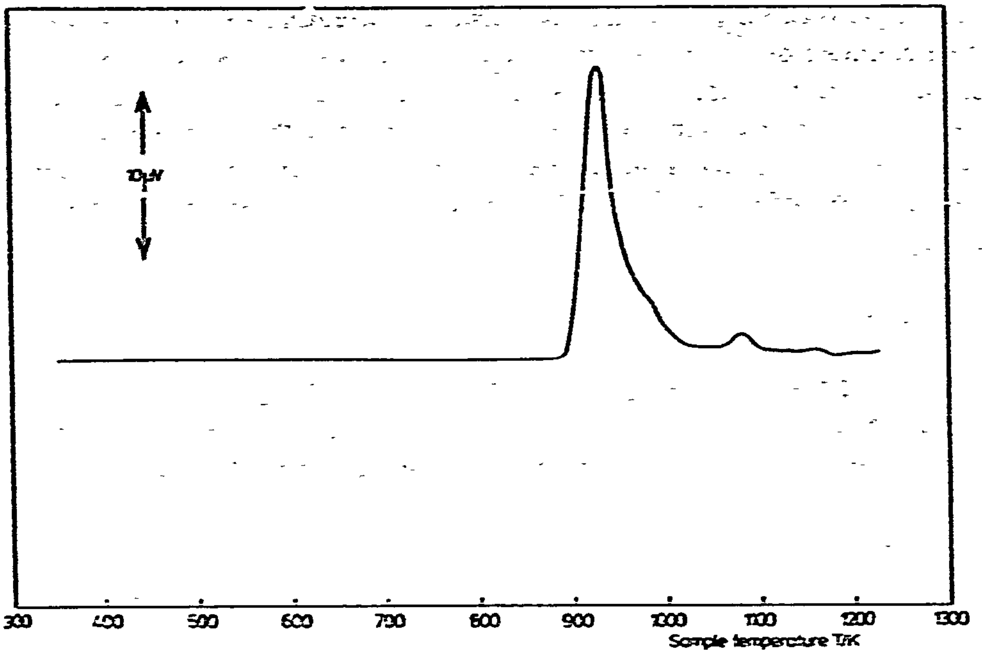

Fig. 5. DTA curve for a mixture containing 10% boron and 90% potassium chromate. Sample weight, 20 mg; heating rate, 5 K min^{-1}; atmosphere of argon, 100 cm^3 min^{-1}.

The experimental values of the exothermicities for mixtures containing 4–7% boron are about 70% of the values predicted on the basis of the equation. The difference of 30% is rather large to be attributed solely to incorrect delineation of the peak areas, and thus, the equation may not be an entire description of the first stage of the reaction.

X-ray analysis showed that potassium chromate is partially consumed in the second reaction stage and that this consumption is greatest for the 7% boron mixture. These results were confirmed by spectrophotometric analysis which also showed that more potassium chromate is consumed under ignition conditions than on controlled heating to the completion of the second exotherm. When mixtures of boron and potassium chromate containing 5–10% boron were heated under non-ignition conditions a single DTA exotherm was observed in the same temperature region as that for the second reaction exotherm with potassium dichromate (see Fig. 5). This shows that the second stage of the pyrotechnic process is the reaction between the boron remaining from the first stage and the potassium chromate which is formed in the first stage. Mixtures of boron and potassium chromate have been ignited under DTA conditions and the observed peak areas are in good agreement with those obtained from DTA ignition experiments carried out with the products from the first reaction stage. The peak areas obtained in the latter experiments are larger than those obtained under non-ignition conditions indicating that the high temperature reaction is more complete in the ignition process. This may account for part of the difference between the total exothermicity obtained under ignition conditions and the value derived from the first and second exotherms.

Mixtures of boron and potassium dichromate containing only 4% boron do not propagate a combustion wave. This may be attributed to the absence of sufficient boron to promote the second stage. Thus, the first stage alone does not self-propagate combustion, it acts as a trigger, and it is the second stage which actually propagates the combustion wave. The second stage reaction can be established independently of the first and mixtures of boron and potassium chromate can be ignited and burn smoothly.

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