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DIFFERENTIAL THERMAL ANALYSIS AND TEMPERATURE PROFILE ANALYSIS OF PYROTECHNIC DELAY SYSTEMS: TERNARY MIXTURES OF SILICON, BORON AND POTASSIUM DICHROMATE

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ABSTRACT

There are two main reaction stages in the pyrotechnic combustion of ternary mixtures of silicon, boron and potassium dichromate. The first stage is the reaction between boron and potassium dichromate. Silicon is involved only in the second reaction stage, which propagates the combustion. The first stage acts as a trigger for the second and, in the absence of boron, mixtures of silicon and potassium dichromate are much more difficult to ignite.

INTRODUCTION

Ternary mixtures of silicon, boron and potassium dichromate are used in pyrotechnic delays [1]. The description "gasless" is usually applied to these mixtures since during combustion less than 10 cm^3 of gas is evolved per g of mixture. It is this aspect which makes differential thermal analysis (DTA) a particularly relevant means of study for these mixtures. The technique is most productive when applied under non-ignition conditions and needs to be complemented by temperature profile analysis to investigate the ignited systems. The application of both techniques in a combined approach to the study of binary mixtures of boron and tungsten with potassium dichromate has already been explored [2,3]. We have now extended the application of these techniques to an investigation of ternary mixtures of silicon, boron and potassium dichromate.

The main concern has been the role of silicon in ternary mixtures prepared from mixtures of boron and potassium dichromate which differ in their ability to sustain combustion. Our earlier work [2] has shown that with binary mixtures containing 5% * or more boron there is a two-stage combustion reaction which is self-propagating, whereas mixtures containing 4%

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* In expressing compositions, % = (weight of component × 100)/weight of mixture.

boron show only the lower temperature reaction stage which does not self-propagate. Increasing the proportion of boron from 5 to 5% is critical to the propagation of combustion and it is the effect of adding silicon to these binary mixtures which has been the focus of interest.

A previous investigation of two ternary mixtures containing (a) 5% silicon, 4% boron, 91% potassium dichromate, (b) 20% silicon, 10% boron, and 70% potassium dichromate by Howlett and May [4] has shown that the initial reaction is between boron and potassium dichromate. The work was carried out using differential scanning calorimetry and was limited to the range from ambient temperature to 773 K. In the present work we have examined the mixtures over a wider temperature range using both ignition and non-ignition conditions to obtain further information on the individual reaction stages.

EXPERIMENTAL

Materials

Silicon was 99% pure (Murex) and had a nominal particle diameter of 2.1 μm (Fisher sub-sieve sizer). Amorphous boron (Trona brand, American Potash and Chemical Corp.) and potassium dichromate (BDH, AnalaR grade), nominal particle diameters 0.8 and 4.6 μm, respectively, were samples of the same materials used previously [2]. Mixtures were prepared by brush-mixing the components once through a 100 mesh sieve and twice through a 200 mesh sieve. Before use the components were sieved through a 200 mesh sieve.

Differential thermal analysis

DTA studies were made using Stanton Redcroft equipment (models DTA 673 and DTA 674). This equipment uses platinum/13% rhodium thermocouples in single stem ceramic heads and furnaces wound with either nichrome or platinum/rhodium wire. The ternary mixtures were studied in dimpled platinum/rhodium crucibles in a downward flow of high purity argon (100 cm^3 min^{-1}). Experiments on binary mixtures of silicon and potassium dichromate were made using quartz crucibles because there was a tendency with these mixtures for molten potassium dichromate to creep in the platinum/rhodium crucibles. The reference material was calcined aluminium oxide. Ignition experiments were carried out using samples weighing 50 mg and a heating rate of 20 K min^{-1}. For the non-ignition experiments the samples weighed 10—20 mg and the heating rate was 10 K min^{-1}.

Temperature profile analysis

Temperature profiles were recorded with platinum—platinum/10% rhodium thermocouples made from wires 0.2 mm in diameter. The thermocouple junctions were embedded in the pyrotechnic mixture which was contained in steel tubes. Minor modifications were made to the experimental procedures described previously [3]. The small hole through the steel tube was replaced by a longitudinal slot 1 mm wide. Two increments of pyrotechnic mixture were used. The first was pressed into the tube by hand and the thermocouple placed in the slot with the junction in contact with the mixture. The second increment was pressed onto the thermocouple by hand and both increments were then pressed with a dead load press at 70 MPa (about 5 ton in.$^{-2}$). The pyrotechnic mixture was ignited with a fuse and the thermocouple signal captured by a transient recorder (Data Laboratories, model DL 905). The instantaneous rate of evolution of heat (power) from the combustion was derived from the temperature profiles using the procedures outlined in ref. 2.

Ancillary measurements

Reaction exothermicities were measured using an adiabatic combustion calorimeter (Gallenkamp, Autobomb) which was calibrated with benzoic acid (BDH, thermochemical grade). The pyrotechnic mixtures were burnt compacted into quartz crucibles in an atmosphere of argon. The mixtures were ignited by passing an electric current through a fine platinum wire in contact with the pyrotechnic mixture. Temperatures were measured using a quartz thermometer (Hewlett—Packard, model 2801 A) with a resolution of 10^{-4} K.

The burning velocity of the pyrotechnic mixtures was measured in the temperature profile experiments. The total length of the pressed column of mixture was measured with a dial gauge (British Indicators). The burning time was recorded using an electronic timer (Venner, model TSA6616) which was started by the electric pulse used to fire the ignition fuse and stopped by the signal from a photocell used to detect burn-through. A small correction was made for the response time of the apparatus. The time between pressing the pyrotechnic mixture in the steel tubes and ignition was 2 h. Some measurements were also made in the absence of a thermocouple. There was no significant difference in the results.

RESULTS

Temperature profile analysis

The temperature profiles shown in Fig. 1 are for ternary mixtures prepared by adding silicon to the binary mixture containing 5% boron and 95% potassium dichromate and also for the binary mixture itself. The effect of adding silicon to the binary mixture is to increase both the initial rate of temperature rise and the maximum burning temperature. For a mixture containing 7.5% silicon the maximum burning temperature was above the melting temperature of the thermocouple (~2000 K).

A more detailed interpretation of the temperature profiles is not straightforward since they differ in fine structure even when recorded for the same

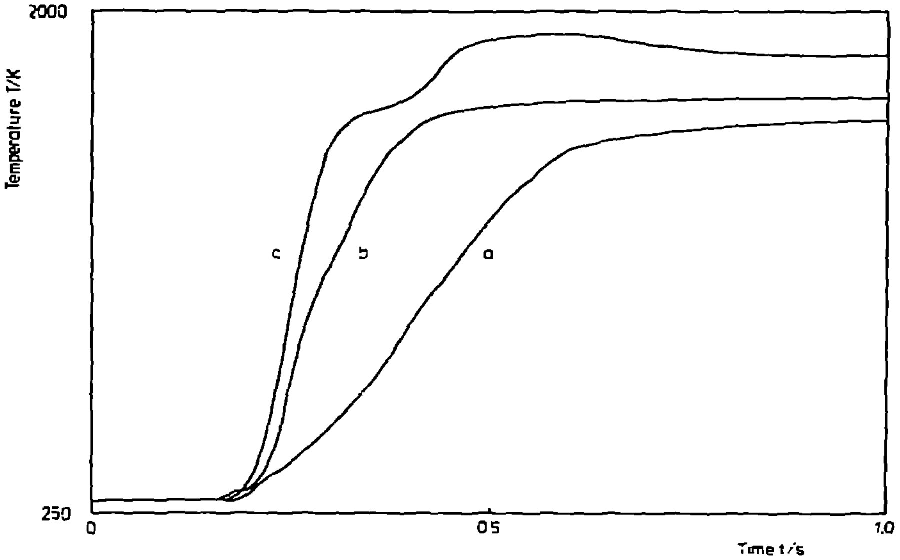


Fig. 1. Temperature profiles for the binary mixture (a) 5% boron and 95% potassium dichromate, and ternary mixtures containing (b) 2.5%, and (c) 5% silicon prepared from the binary mixture.

mixture. These differences give rise to marked variations in the power functions which depend not only on the temperature profile but also on the first and second derivatives. Most of the power functions obtained with the present mixtures show two incompletely resolved exotherms. The temperatures of the peak maxima are in the ranges 600—900 K and 800—1100 K, respectively. An example of a power function for each of the ternary mixtures is shown in Fig. 2. In this figure $G = w/c$, where w is the power and c is the heat capacity. The power functions show less evidence of noise than those reported in earlier work. This is due both to an increased amount of smoothing introduced into the numerical processing and to the changes in the experimental technique.

The ternary mixtures prepared by adding silicon to the binary mixtures containing 4% boron and 96% potassium dichromate have been found to propagate combustion readily. The temperature profiles are similar to those already described. The power function for the ternary mixture containing 2.5% silicon is shown in Fig. 3. The two exotherms have peak maxima at 700 and 1100 K.

Differential thermal analysis

The DTA curves for the ternary mixtures recorded under ignition conditions closely resemble those recorded for the binary mixtures of boron and potassium dichromate [2]. They show a large exotherm starting at 660 K with a measured temperature rise of about 100 K. An example is shown in Fig. 4. At high sensitivity there is a pre-ignition exotherm and an endotherm corresponding to the fusion of potassium dichromate.

The DTA curves recorded under non-ignition conditions for ternary mix-

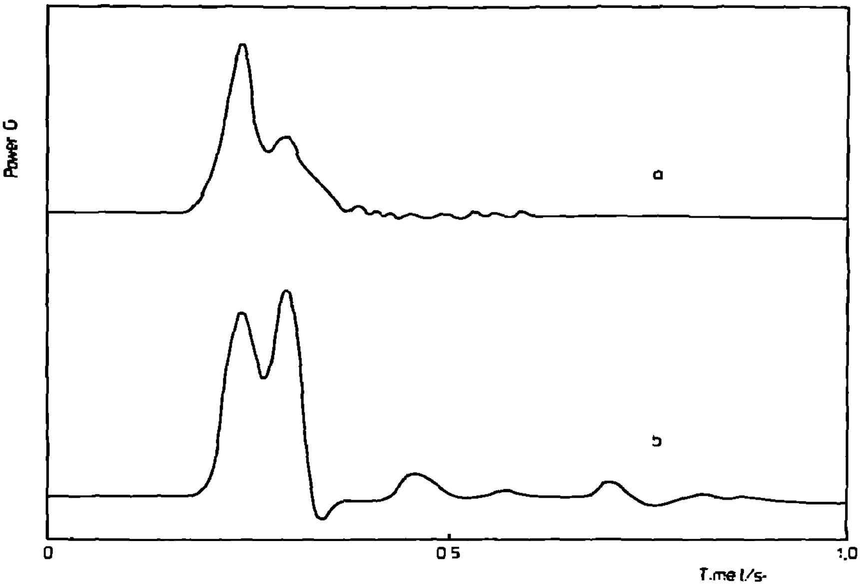


Fig. 2. Power functions derived from temperature profiles for the ternary mixture containing (a) 2.5%, and (b) 5% silicon prepared from the binary mixture containing 5% boron and 95% potassium dichromate.

tures containing 4, 6 and 10% silicon prepared by adding silicon to the mixture containing 4% boron and 96% potassium dichromate are shown in Fig. 5. The curve for the binary mixture with its single main exotherm is also shown for comparison. All the curves show an exotherm starting at 650 K, with a peak maximum at 690 K on which is superimposed the endotherm of fusion of potassium dichromate. The curves for the ternary mixtures also

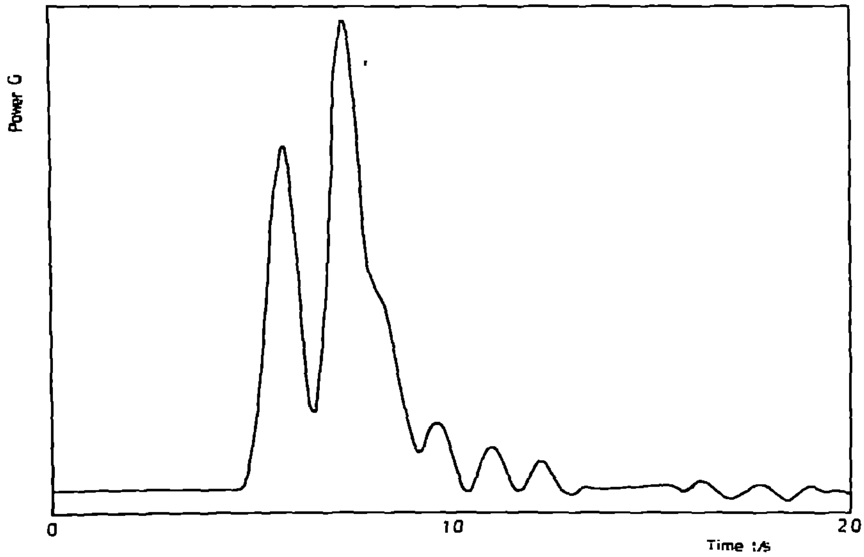


Fig. 3. Power function for the ternary mixture containing 2.5% silicon prepared from the binary mixture containing 4% boron and 96% potassium dichromate.

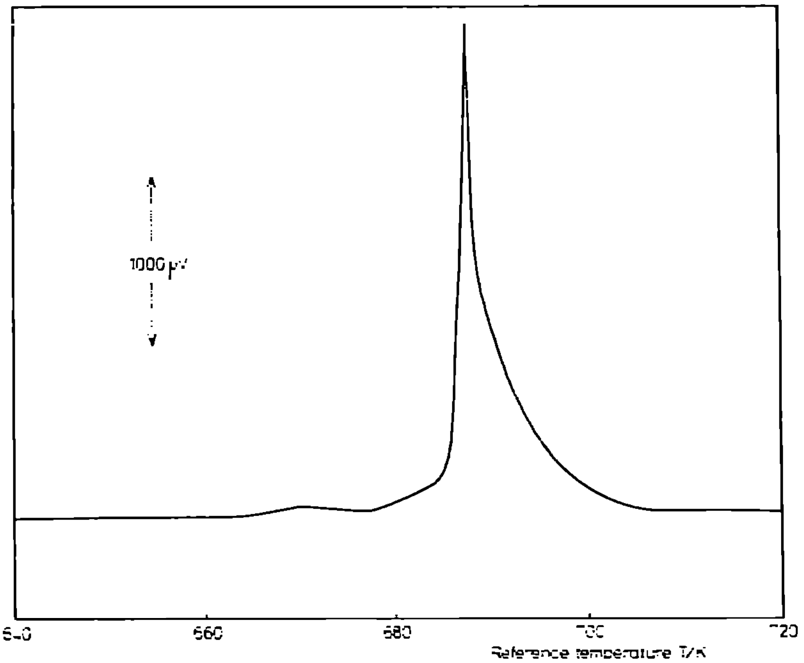
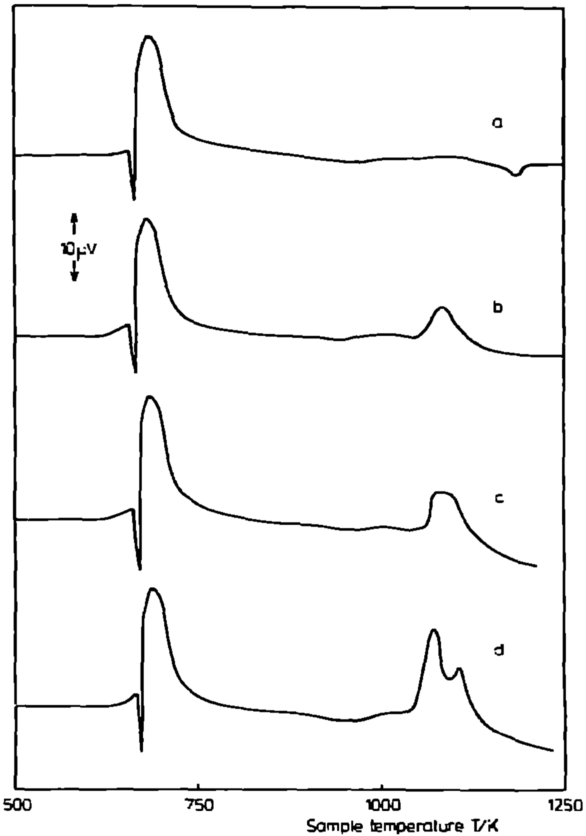


Fig. 4. DTA curve for a ternary mixture containing 5% silicon prepared from the binary mixture containing 4% boron and 96% potassium dichromate, recorded under ignition conditions. Sample weight 50 mg; heating rate 20 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

show a second exotherm with an extrapolated onset temperature of 1050 K. Quantitative DTA measurements show that the area of the high temperature exotherm increases as the proportion of silicon is increased. In contrast, the presence of silicon does not affect the low temperature exotherm. With mixtures containing 10% or more silicon the high temperature exotherm is partially resolved into two peaks.

Figure 6 shows the DTA curves recorded under non-ignition conditions when silicon is added to binary mixtures containing 5 and 7% boron. Curve (a) is for the binary mixture containing 5% boron and shows a high temperature exotherm, albeit very poorly defined. Curve (b) shows that the area of the exotherm is considerably increased when silicon is added to the binary mixture. A similar increase in area is observed when silicon is added to a binary mixture containing 7% boron (curves c and d). For this binary mixture the high temperature exotherm is clearly resolved and has an extrapolated onset temperature of 950 K. The high temperature exotherm for all these mixtures occurs at a temperature of about 100 K lower than that observed for ternary mixtures prepared from a 4% boron mixture.

The DTA curves have also been recorded for binary mixtures of silicon and potassium dichromate. Under non-ignition conditions they show the endotherm of fusion of potassium dichromate and a large well-defined exotherm with an extrapolated onset temperature of 1050 K. There was no evidence of a low temperature exotherm and thermogravimetry indicated that little decomposition of the potassium dichromate (<5% weight loss)



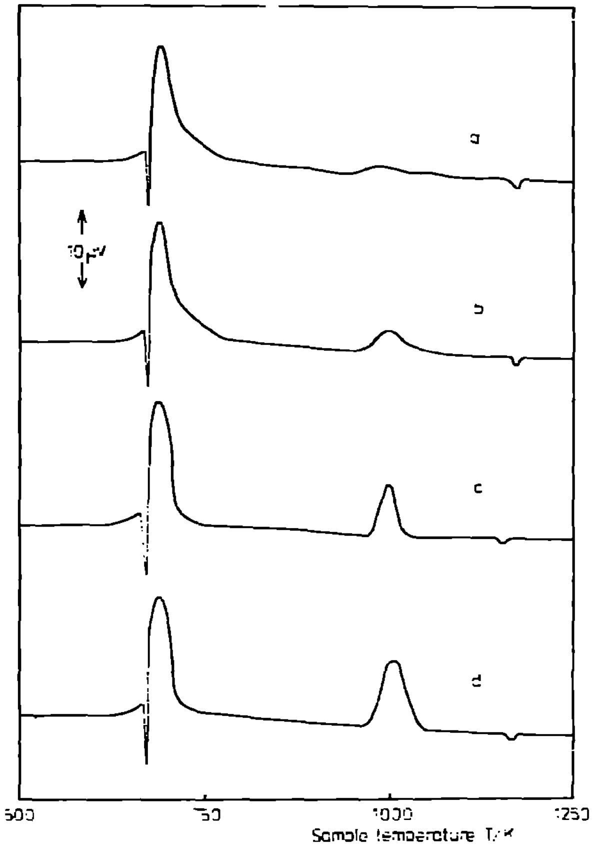


Fig. 5. DTA Curves for the binary mixture (a) 4% boron and 96% potassium dichromate, and ternary mixtures containing (b) 4%, (c) 6%, and (d) 10% silicon prepared from the binary mixture, recorded under non-ignition conditions. Sample weights 10—20 mg; heating rate 10 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

Fig. 6. DTA curves for the binary mixtures containing (a) 5% and (c) 7% boron and potassium dichromate and the corresponding ternary mixtures containing 5% silicon (b) and (d), recorded under non-ignition conditions. Sample weights 10—20 mg; heating rate 10 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

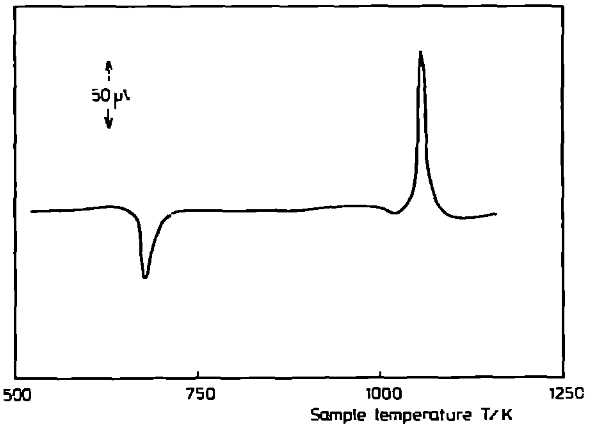


Fig. 7. DTA curve for the binary mixture containing 7% silicon and 93% potassium dichromate, recorded under non-ignition conditions. Sample weight 20 mg; heating rate 10 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

TABLE 1

Reaction exothermicities of ternary mixtures prepared by adding silicon to a binary mixture containing 5% boron and 95% potassium dichromate

% Silicon	2	4	6	8	10	20	25	30
Exothermicity $(kJ\,g^{-1})$ *	2.41 ± 0.02	2.98 ± 0.02	3.31 ± 0.02	3.31 ± 0.02	3.31 ± 0.02	3.27 ± 0.04	3.31 ± 0.03	3.12 ± 0.04

* The units refer to 1 g of mixture.

TABLE 2

Reaction exothermicities of binary mixtures of boron and potassium dichromate

% Boron	5	6	7	8	10	15	20	25	30
Exothermicity $(kJ\,g^{-1})$ *	2.33 ± 0.02	2.66 ± 0.04	3.10 ± 0.02	3.35 ± 0.02	3.59 ± 0.02	4.02 ± 0.03	4.34 ± 0.06	4.27 ± 0.02	4.13 ± 0.05

* The units refer to 1 g of mixture.

TABLE 3

Reaction exothermicities of binary mixtures of silicon and potassium dichromate

% Silicon	15	17.5	20	22.5	25	27.5	30	50
Exothermicity $(kJ\,g^{-1})$ *	3.07 ± 0.02	3.09 ± 0.02	3.25 ± 0.02	3.21 ± 0.03	3.27 ± 0.02	3.08 ± 0.03	3.08 ± 0.03	2.45 ± 0.02

* The units refer to 1 g of mixture.

occurred before the onset of this exotherm. The curve for the mixture containing 7% silicon and 93% potassium dichromate is shown in Fig. 7.

Reaction exothermicities

The calorimetric values of the exothermicities of the ternary mixtures are shown in Table 1. The results of measurements on the binary mixtures of boron and silicon with potassium dichromate are shown in Tables 2 and 3. For the silicon system there is a maximum in the range 20—25% silicon, in agreement with the results of Spice and Staveley [5]. We have not investigated the maximum at 55% silicon also reported by these authors.

DISCUSSION

Temperature profile analysis has shown that there are two main exothermic reaction stages in the pyrotechnic combustion of ternary mixtures of silicon, boron and potassium dichromate. For those mixtures prepared from the 4% boron—96% potassium dichromate mixture, it is the presence of silicon which is responsible for the propagation of the combustion. DTA under non-ignition conditions confirms the presence of a second reaction stage at about 1100 K which is absent from the binary mixture. This stage involves the reaction between silicon and potassium chromate, which is formed in the first stage reaction between boron and potassium dichromate. Binary mixtures containing sufficient boron to propagate combustion show an exotherm at 970 K and it might be expected that the addition of silicon would produce another exotherm at 1100 K. However, this has not been resolved. DTA shows a single exotherm at 1000 K with a greater area than that observed for the binary mixtures which is consistent with the increased exothermicity. This single peak becomes partially resolved for mixtures containing 10% or more silicon. DTA curves recorded for mixtures of silicon and potassium chromate show a broad exotherm starting at about 950 K although it is poorly defined and not readily reproducible.

The present work confirms the conclusion of Howlett and May [4] that silicon does not take part in the first stage of the combustion reaction. This stage, involving boron and potassium dichromate, acts as a trigger for the second which propagates the combustion. It has already been shown that for binary mixtures of boron and potassium dichromate the second stage involves the reaction between the excess of boron remaining from the first stage and potassium chromate [2]. For the ternary mixtures the second stage is more complex since it involves silicon and in some cases boron, depending on the initial composition. The calorimetric results indicate that the exothermicity of the 5% boron mixture can be increased by a maximum of about 40% by the addition of only 6% silicon. Further addition of silicon does not significantly change the exothermicity until the proportion reaches more than 25%, when the exothermicity decreases. In contrast, the maximum exothermicities of the binary mixtures of both boron and silicon with potassium dichromate are more sharply defined in the range 20—25% fuel

TABLE 4

The effective thermal diffusivities of binary and ternary mixtures of silicon, boron and potassium dichromate

% Boron in the binary mixture	5	5	5	4	4
% Silicon in the ternary mixture	—	2.5	5	2.5	5
Burning velocity ($10^3\ v\ \mathrm{m}^{-1}\ \mathrm{sec}^{-2}$)	4.53 ± 0.36	9.06 ± 0.44	17.2 ± 0.6	4.21 ± 0.10	7.87 ± 0.30
$10^2\ t^*$ (sec)	6.1 ± 2.5	1.97 ± 0.67	1.26 ± 0.70	7.12 ± 0.58	2.90 ± 0.37
Thermal diffusivity ($10^6\ D\ \mathrm{m}^{-2}\ \mathrm{sec}^{-1}$)	1.0 ± 0.5	1.6 ± 0.6	6.7 ± 2.1	1.3 ± 0.1	1.8 ± 0.2

(Tables 2 and 3). For ternary mixtures containing more than 5% boron the addition of silicon has less effect on the exothermicity. The ignition temperature of the ternary mixtures is about 660 K. In the absence of boron, mixtures of silicon and potassium dichromate are much more difficult to ignite and at ambient temperatures 15% silicon is needed for the combustion to self-propagate. DTA indicates an ignition temperature nearly 400 K higher than that for mixtures containing boron.

THERMAL DIFFUSIVITY OF PYROTECHNIC MIXTURES

The thermal diffusivity D is defined by the equation

$$D = k/\sigma c$$

where k, σ and c are the thermal conductivity, density and heat capacity, respectively. For pyrotechnic systems there is an almost complete lack of thermal diffusivity data notwithstanding the importance of this parameter in discussing heat transfer in these systems. The main source of practical difficulty lies in the measurement of the thermal conductivity. The value $k = 0.42$ W m^{-1} K^{-1} (10^{-3} cal sec^{-1} cm^{-1} K^{-1}), which is often used for pyrotechnic systems, appears to be that reported by Hill [6] in 1954 for mixtures of iron and potassium permanganate. In ref. 2 we defined a time $t^* = Dv^{-2}$ which could be derived from the exponential rise and decay of the temperature excess U in the inert initial and final regions of the temperature profile. It was shown that $t^{*-1} = \alpha_1 + \alpha_2$ and we may assign α_1^{-1} and $-\alpha_2^{-1}$ to the rise time $t_r = (\mathrm{d}\ln U/\mathrm{d}t)^{-1}$ and the decay time $t_d = -(\mathrm{d}\ln U/\mathrm{d}t)^{-1}$ of the inert initial and final regions, respectively. Thus it is possible to obtain the thermal diffusivity if an independent measurement of the burning velocity v is available. In principle, the thermal diffusivity derived in this way is a mean effective value and relates to reactants and products over the temperature ranges of the inert regions. However, in the present experiments the rise time is much less than the decay time ($t_r/t_d < 0.01$) and $t^{*-1} = t_r^{-1} - t_d^{-1} \approx t_r^{-1}$ so that the thermal diffusivity refers to the reactants over the range ambient temperature to ignition (about 660 K). Results for some of the mixtures considered in this paper are listed in Table 4, where the errors are the standard deviations. With one exception there is agreement between the results within twice the total standard deviations, giving a mean effective thermal diffusivity of about 1.4×10^{-6} m^2 sec^{-1} for these mixtures.

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