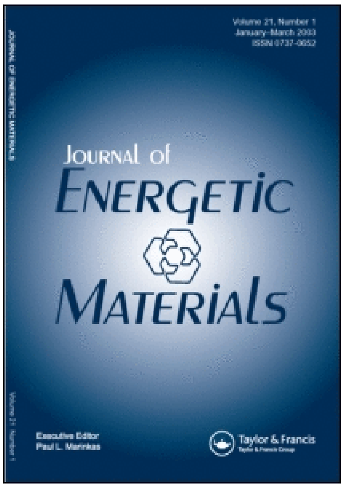

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Whelan, Daniel J. , Maksacheff, Michael , Pletikapa, Branka and de Yong, Leo V.(1988) 'Kinetics and thermochemistry of the boron-fuelled pyrotechnic compositions BLC 190 and BLC 181 at their ignition temperatures', Journal of Energetic Materials, 6: 3, 201 — 214

To link to this Article: DOI: 10.1080/07370658808012554

URL: http://dx.doi.org/10.1080/07370658808012554

KINETICS AND THERMOCHEMISTRY OF THE BORON-FUELLED PYROTECHNIC COMPOSITIONS BLC 190 AND BLC 181 AT THEIR IGNITION TEMPERATURES

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ABSTRACT

Around 700 K, the pyrotechnic compositions BLC 190 (boron : red lead, 10 : 90) and BLC 181 (boron : red lead : chromic oxide, 10 : 80 : 10) undergo exothermic thermal decomposition reactions which follow first order kinetics. The reaction of BLC 190 is faster than that of BLC 181 but the energies of activation, ca. 446 kJ mol^{-1}, and the heat output per unit mass of oxidant, Pb_3O_4, ca. 1000 J g^{-1}, are very similar suggesting that the reactions of each of these formulations follow identical pathways. The product of the reaction from BLC 190 has been identified as lead tetraborate or a closely related compound.

Journal of Energetic Materials vol. 6, 201-214 (1988)

Published in 1988 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Although there have been several investigations of the behaviour of boron-fuelled pyrotechnic compositions under slow, controlled ignition conditions [1], there have been very few studies made of the kinetics and thermochemistry of this behaviour. This paper seeks to address this situation, reporting on the kinetics and thermochemistry of two pyrotechnic compositions, BLC 190 and BLC 181, as studied by isothermal differential scanning calorimetry.

BLC 190 was originally formulated by Bentley and Elischer [2] and consists of an intimate mixture of amorphous boron (10% by weight) and red lead, Pb_3O_4 (90% by weight). Its temperature of ignition occurs at 682 K (uncorr.) in the MRL "Temperature of Ignition" Apparatus. The composition resulting from admixture of BLC 190 (95% by weight) and tetrazene (5% by weight) has been adopted as the primer composition in M42F1 percussion cap assemblies.

The composition, BLC 181, is a modification of BLC 190, consisting of boron (10% by weight), red lead (80% by weight) and a compatible moderator, chromic oxide, Cr_2O_3 (10% by weight) [3]. Its temperature of ignition occurs at 675 K and, like BLC 190, it sustains ignition from the output of conventionally filled M42 and M42F1 percussion caps in the recently-developed MRL Ignition Stand-Off Test [4].

In the present study, it has been found that, around 700 K, both BLC 190 and BLC 181 undergo exothermic reactions which follow first-order kinetics. The reaction of BLC 190 is faster than that of BLC 181 but the energies of activation, ca. 446 kJ mol^{-1}, and the exothermicities (heat output per unit mass of oxidant, Pb_3O_4) are very similar, ca. 1000 J $(g, Pb_3O_4)^{-1}$.

EXPERIMENTAL

1. Materials

Boron was a technical grade, amorphous powder from Trona-Kerr McGee Corp, Oklahoma, USA; it was washed and dried before use. SEM revealed that the particle size of this material was "sub-micron".

Red lead, Pb_3O_4, and chromic oxide, Cr_2O_3, were both May and Baker analytical grade reagents which were ball-milled individually before use. The mean particle size of Pb_3O_4 was 6-8 µm; that of Cr_2O_3, 10-12 µm. The DSC traces from B, from Pb_3O_4 and from Cr_2O_3 have been previously described [5]. Below 750 K, the contributions of the individual components to a non-isothermal DSC trace is negligible [3,5].

Batches of BLC 190 and of BLC 181 were prepared in a standard way by repetitive dry mix - sieving to produce homogeneous blends of the ingredients.

2. Differential Scanning Calorimetry

Thermochemical measurements were obtained using a Perkin-Elmer DSC-2C Differential Scanning Calorimeter controlled by a Perkin-Elmer Model 3600 Data Station with appropriate software.

All samples were accurately weighed on a Mettler ME30 Microanalytical Balance directly into aluminium sample pans and lids placed (but not crimped) over the samples [6].

The sample and reference compartments of the calorimeter were continuously purged with nitrogen gas throughout the DSC scans, the nitrogen flow rate typically being 20-25 ml min^{-1}.

Temperature calibration was carried out using NBS thermal analysis standards, indium (m.p. 429.8 K, heat of fusion 28.6 J g^{-1} [7]) and zinc (m.p. 692.6 K [7]).

Samples of BLC 190 and BLC 181 were weighed on the microbalance before and after each DSC run. No change in mass was observed as a result of the reaction processes from either sample.

3. Isothermal DSC Traces from BLC 190 and BLC 181

Isothermal DSC traces were carried out following the procedure described in the Perkin Elmer Software Package "ISOTHERMAL" using thermally-balanced sample and reference compartments. From non-isothermal DSC traces, it was apparent that BLC 190 and BLC 181 were quite stable at temperatures below 650 K and that slow but obvious decomposition appeared to occur only above 675-680 K.

Preliminary experiments suggested that the progress of the reaction could be conveniently followed by DSC studies over the "nominal" temperature range 690-705 K for BLC 190 and 695-715 K for BLC 181.

In a typical experiment, the sample (in an aluminium sample pan) was loaded into the sample compartment of the calorimeter, which had been previously heated to a temperature of 80 K below the temperature chosen for the study. The sample was allowed to equilibrate at this temperature (ca. two minutes) and then the temperature of the calorimeter raised rapidly (at 80 K min^{-1}) to the final temperature. The progress of the reaction was followed by observing the change in output of heat (dQ/dt) with time (t).

The analyses of the experimental results obtained from BLC 190 are described in detail, below; similar procedures were also applied to the results from BLC 181.

A typical isothermal thermogram for a run carried out on BLC 190 at 705 K is given in Fig. 1 - the output being "corrected" for the output associated with "blank runs" at 705 K. In Fig. 2, the same data is reproduced in an alternative form, viz. heat output vs. time.

From an analysis of the data presented in Fig. 1, one obtains the amount of fractional decomposition, α , at any time, t, by dividing the area under the curve from t=0 to t by the total area under the curve (which is a measure of the heat of reaction of the overall process).

The curve follows the first order rate law

$$\frac{d}{dt}\alpha = k_1 (1 - \alpha) \qquad (1)$$

(with $k_1 = 0.172 \pm 0.010\ \mathrm{min}^{-1}$ at 705 K, for BLC 190) from a period 1.3 minutes after the commencement of the experiment, right through to a period of 22 minutes (5.5 half-lives or 97.7 per cent reaction). It has been suggested that the initial period (1.3 min, 78 s) recorded over the DSC run is typical of the time taken for the system to come to thermal equilibrium under the conditions of this experiment.

Whether this initial stage of the reaction is really due to "thermal lag" or not is debatable. It is possible that this period is also associated with "pre-steady state reaction" conditions where the reactants, Pb_3O_4 and boron, interact across their crystal boundaries, forming reactive centres or nuclei from which the pyrotechnic reaction ultimately proceeds [8,9], in this case following first-order kinetics.

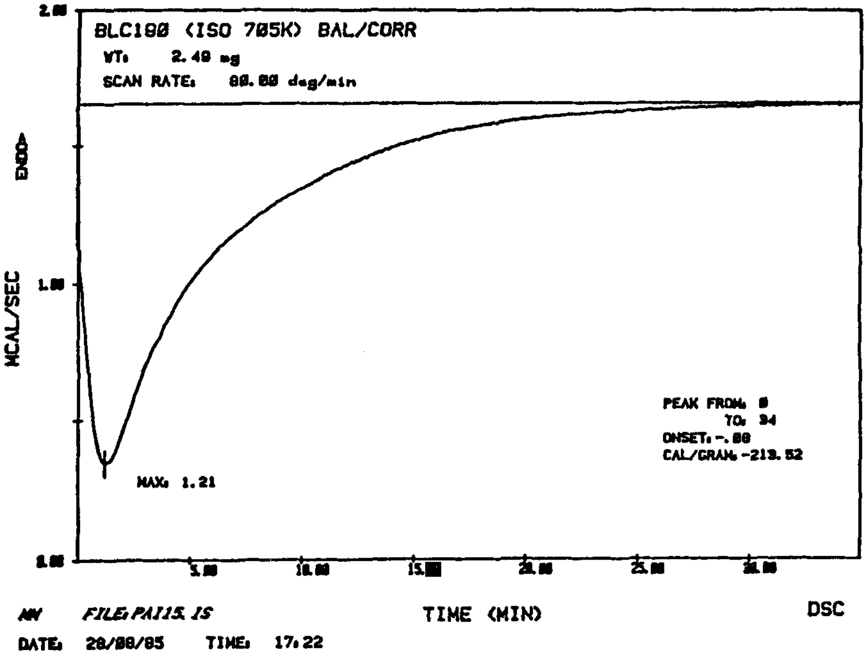

Fig 1. DSC trace of BLC 190 under isothermal conditions at 705 K (Al sample pans, nitrogen atmosphere).

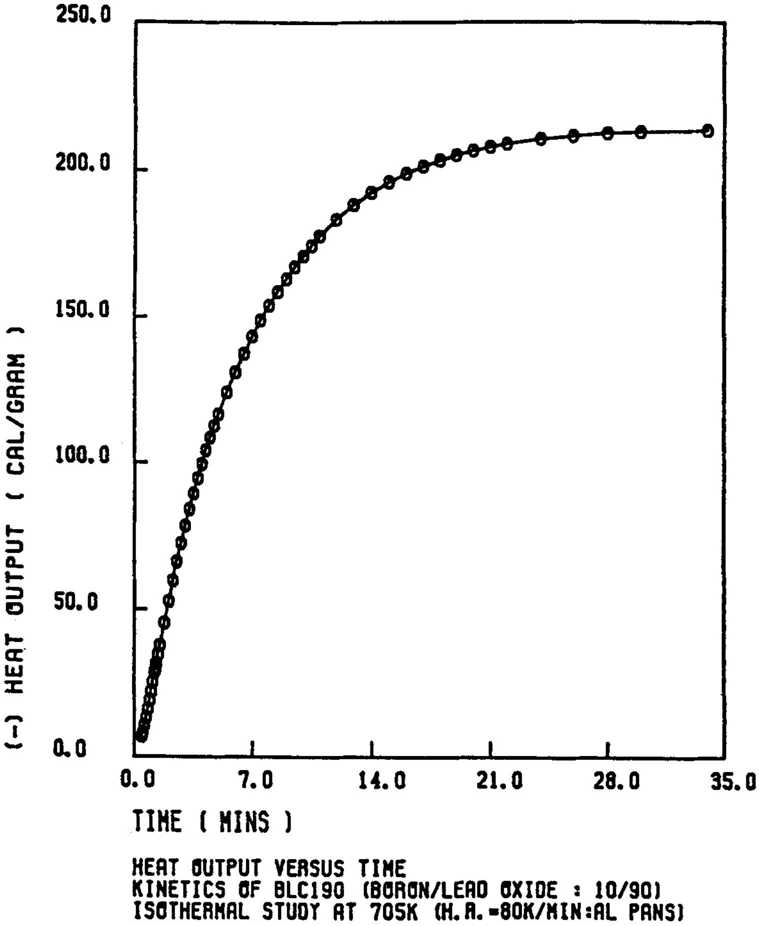

Fig 2. Heat output from BLC 190 under isothermal conditions at 705 K (Al sample pans, nitrogen atmosphere).

Runs carried out at nominal temperatures of 690 K, 695 K, 700 K and 705 K, after this "pre-steady state" stage, all followed the first-order rate law described by eq 1. The calculated first-order rate constants are given in Table 1.

An Arrhenius plot, ln k_1 vs T^{-1}, of these data gave a reasonable straight line corresponding to

$$E^* = 447 \text{ kJ mol}^{-1}, \quad \log_{10} A \ (s^{-1}) = 30.56$$

coefficient of determination = 0.921.

The linearity of this Arrhenius plot from which these parameters were determined, however, is much better than the coefficient of determination (0.921) indicates; in the determination of this coefficient, calculations were based on the "nominal value" of the abscissa (T^{-1}), no weight being given to the effect of the error-bars on this variable.

From the area under the isothermal DSC traces, the heat of reaction was found to be 872 ± 63 J g^{-1} (208 ± 15 cal g^{-1}) or 970 ± 70 J $(g, Pb_3O_4)^{-1}$.

The thermal decomposition of BLC 181 over the temperature range 698-713 K also proceeded with first order kinetics, albeit at a slower rate (Table 2) than that observed with BLC 190. An Arrhenius plot of the data for BLC 181 yielded

$$E^* = 445 \text{ kJ mol}^{-1}, \quad \log_{10} A \ (s^{-1}) = 30.11$$

coefficient of determination = 0.998.

The heat output of this reaction was found to be 810 ± 45 J g^{-1} corresponding to 1010 ± 60 J $(g, Pb_3O_4)^{-1}$

TABLE 1

Kinetics of Thermal Decomposition of BLC 190 as studied by Isothermal DSC between 690 K and 705 K

Temperature, K (nominal)	Temperature, K (actual)	Rate Constant 1st order, k_1 (min^{-1})		
690	690 ± 2.5	0.0212,	0.0295,	0.0378
695	695 ± 0.8	0.0656,	0.0709	
700	700 ± 0.4	0.0830,	0.0866,	0.0903
705	705 ± 0.5	0.1550,	0.1720	

Activation Energy, E* (kJ mol^{-1})	447.2
Preexponential $\log_{10} A$ (s^{-1})	30.56
Coefficient of determination	0.921
Calc. k_1 at 705 K (min^{-1})	0.1602

TABLE 2

Kinetics of Thermal Decomposition of BLC 181 as studied by Isothermal DSC between 698 K and 714 K

Temperature, K (actual)	Rate Constant 1st order, k_1 (min^{-1})	
698.5	0.044,	0.045
703.4	0.073,	0.076
708.3	0.126	
713.3	0.215,	0.220

Activation Energy, E* (kJ mol^{-1})	445
Preexponential $\log_{10} A$ (s^{-1})	30.11
Coefficient of determination	0.998
Calc. k_1 at 705 K (min^{-1})	0.0871

The agreement of the experimentally derived activation energies for BLC 190 and BLC 181 was surprisingly close. Although one may have expected them to be very similar, the systematic errors associated with each set of measurements and the random errors associated with individual measurements suggest that an error in E* for each formulation of ± 3 per cent (± 14 kJ mol^{-1}) would not have been unexpected.

The fact that the activation energies are so close and, under identical reaction conditions, the exothermicities (heat output per unit mass of oxidant, Pb_3O_4) so similar suggests that the two formulations undergo slow, controlled ignition by similar pathways.

DISCUSSION

1. The Chemistry of BLC 190 and BLC 181

In a study such as this, one is entitled to ask :

What is the chemical reaction taking place in this system?

and

What is the significance of the kinetic data?

The study reported here is that of an exothermic solid-state reaction between Pb_3O_4 and B, where the boron is present in considerable molecular excess. It may be for this reason that the observed reaction

$$B + Pb_3O_4 \rightarrow \text{Products + Heat}$$

appears to proceed by first order kinetics. Alternatively, the first order dependence may be attributed to a simple, but as yet unidentified, unimolecular reaction which is rate determining.

The role of chromic oxide has not been considered previously. Below 860 K, the upper limit of our investigations, no reaction occurred between B and Cr_2O_3, at least short term. At the same time, below ca. 730 K, no reaction occurs in the Pb_3O_4/Cr_2O_3 system although, above ca. 750 K, thermal decomposition of Pb_3O_4 occurs [3,5] according to the equation

$$2\ Pb_3O_4 \rightarrow 6\ PbO + O_2$$

From Tables 1 and 2, it is apparent that the rate of reaction for BLC 190 is faster than the rate of reaction for BLC 181 and, as the activation energies and exothermicities (per unit mass of oxidant) are very similar, Cr_2O_3 is probably functioning as a moderator as well as a diluent. Were it acting solely as a diluent, the ratio of reaction rates for BLC 190 to that for BLC 181 would be in the ratio of the relative amounts of Pb_3O_4 in the respective formulations, viz. 9 : 8 or 1.1, under the same conditions. On the other hand, the ratio of the rate constants, calculated at 705 K, is ca. 1.8, suggesting that Cr_2O_3 plays a moderating role - probably impeding the access of the oxidant Pb_3O_4 to the fuel. This is confirmed by other work involving not only BLC 190 and BLC 181 but also related formulations, BLC 172 and BLC 145 [3].

However, no further investigation of the stoichiometry of these reactions has been undertaken, per se, save that there was no loss of mass from the reaction pans during the decomposition of BLC 190 and of BLC 181.

In their original publication on BLC 190, Bentley and Elischer [2] reported that maximum burning rate for their delay composition occurred in mixtures containing 8-12 per cent B. This is an interesting result but it was one based on end-use practicalities rather than chemical considerations.

As to the products from this reaction, it had been tacitly assumed at the outset of this investigation that the products from the thermal decomposition of BLC 190 near 700 K would be B_2O_3 and PbO or Pb.

However, the infra-red absorption spectrum (KBr disc) of the reaction products from BLC 190 showed no evidence for the presence of boron oxides as such but showed broad bands at 1350 (s), 950 (s) and 650 (m) cm^{-1} which are apparently characteristic of borate salts [10].

To investigate this further, lead diborate ($PbO.2B_2O_3$ or PbB_4O_7) was synthesised from stoichiometric amounts of PbO (or Pb_3O_4) and H_3BO_3 at 900-950°C (Pt crucible) [11]. Its infra-red spectrum (KBr disc) was found to have bands centered about 1380 (s), 950 (br) and 650 (m) cm^{-1}. This result supports the suggestion that the reaction products from BLC 190 at around 700 K are salts based on lead borate.

That the kinetic model followed by both BLC 190 and BLC 181 has turned out so simply was surprising. In a recently published study on the effect of particle size on the kinetics of reaction between MgO and Al_2O_3, Beretka and Brown [12] found that the kinetics of spinel formation, described by the equation

$$MgO + Al_2O_3 \rightarrow Mg\,Al_2O_4,$$

depend on the particle size of reactants. For small-sized (ca. 5 μm) reactants, the reaction follows a rate law consistent with Avrami-Erofeev nucleation kinetics with a plot of

$$\ln \ln (1 - \alpha)^{-1} \quad vs \quad \ln t$$

being linear. For larger-sized reactants (45-55 μm), far less complicated linear first-order kinetics were followed.

It is quite possible that a similar trend could be occurring with BLC 190 and BLC 181 but this has not been pursued.

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