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TEMPERATURE DEPENDENCE OF THE BURNING VELOCITY OF GASLESS PYROTECHNICS

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ABSTRACT

Burning velocity measurements have been made on three gasless pyrotechnic mixtures over an extended range of ambient temperatures. The results have been used to obtain the activation energies of the combustion process. The values obtained (typically less than 50 kJ mol^{-1}) are low compared with those under non-ignition conditions, where it seems that a different rate-determining step prevails.

INTRODUCTION

The temperature dependence of the burning velocity is relevant to the application of pyrotechnic systems and to a more detailed consideration of the pyrotechnic combustion process itself. For practical applications, it is common to restrict assessment to measurements over a limited range of temperatures only. In the present paper our concern is with the evaluation of burning velocity data obtained for a wider range of ambient temperatures (195–561 K). Measurements have been made on three pyrotechnics: 50% tungsten–50% potassium dichromate, 5% boron–95% potassium dichromate and 7% boron–93% molybdenum trioxide. The above percentage compositions are expressed as follows: composition (%) = weight of component × 100/weight of mixture.

EXPERIMENTAL

The boron was amorphous grade, 90%–92% pure (Trona Brand, American Potash and Chemical Corporation) and had a nominal particle diameter of 1 μm measured with the Fisher Sub-sieve Sizer. Tungsten powder (nominal particle diameter, 1.2 μm) was obtained from Murex Ltd. Potassium dichromate and molybdenum trioxide were AnalaR grade (BDH) and were ball-milled to particle diameters of 4 μm and 2.5 μm respectively. The compo-

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nents were sieved separately through a 200 mesh (75 μm) sieve before use. The mixtures were made by brush mixing the weighed components once through a 100 mesh (150 μm) sieve and twice through a 200 mesh sieve. The mixtures were burnt in steel tubes 38 mm long and of internal diameter 6.4 mm. A dead-load press was used to give a pressing load of 80 MPa (5 tonf in^{-1}). The dwell time of the drift was 30 s. Four flat-ended increments each 6 mm long were pressed into the steel tubes and the total length of the column was measured with a dial comparator (British Indicators Ltd.). The pressed mixtures were ignited by an E-type fuse. Burning times were recorded using an electronic timer (Venner Ltd., model TSA 5534). The timer was started by an electrical pulse derived from that used to fire the fuse. Burn-through was detected with a photocell from which a signal was derived to stop the timer. A small correction was made for the response time of the apparatus. Temperatures below room temperature were obtained by cooling the pressed pyrotechnic mixtures in either solid carbon dioxide or brine–ice mixtures after first sealing the steel tubes. Temperatures above room temperature were obtained using a small furnace to heat the steel tubes. The effective ambient temperature was recorded using fine precious metal thermocouples inserted into the pyrotechnic mixture.

RESULTS AND DISCUSSION

We have evaluated the burning velocity data using the approximate but algebraically simple theory of propagation originally developed by Zel' dovich and Frank-Kamenetskii [1] for laminar flame propagation in gases. It is assumed that the activation energy is large so that the reaction develops only within a narrow temperature range close to the maximum adiabatic temperature T_m. For reactions in the solid state we may express the kinetic law in the form $d\lambda/dt = Af(\lambda)\exp(-E/RT)$ where λ is the fractional extent of reaction, A is the pre-exponential factor and E is the activation energy. Results from temperature profile studies [2,3] indicate that the isothermal kinetic law may be approximated by a first-order expression, i.e. $f(\lambda) = (1-\lambda)$. The corresponding solid state burning velocity is given by

$$v^2 = 2AD\frac{1}{\Delta T_{ad}^2}\left(\frac{RT_m^2}{E}\right)^2\exp\left(\frac{-E}{RT_m}\right) \tag{1}$$

where ΔT_{ad} is the adiabatic temperature rise and D is the thermal diffusivity of the reactant mixture. From eqn. (1) we would expect an almost linear relationship between $\ln v$ and T_m^{-1}:

$$2\frac{d\ln v}{dT_m^{-1}} = -\frac{E}{R}\left(1+\frac{4RT_m}{E}\right) = -\frac{E_{app}}{R} \tag{2}$$

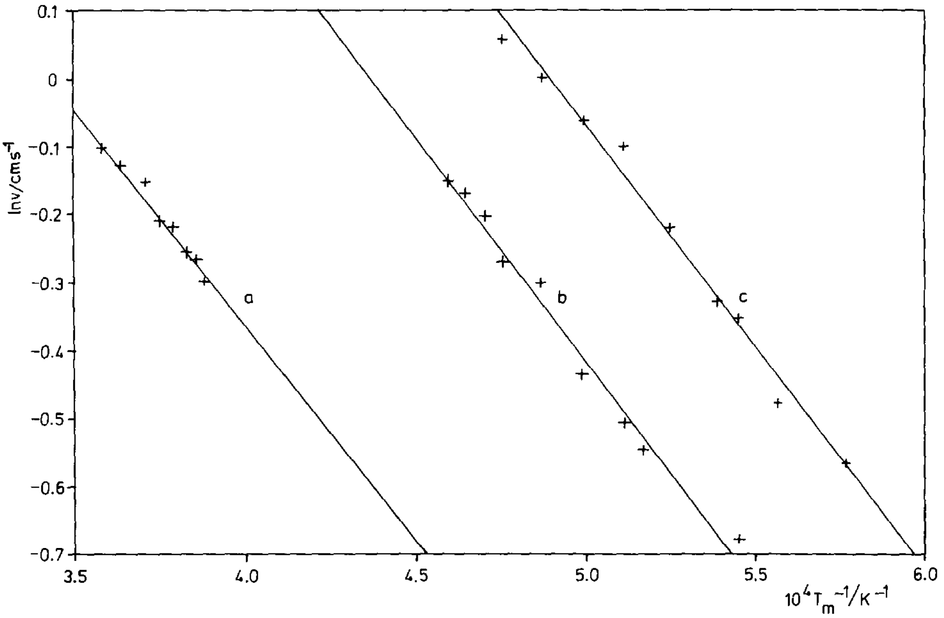

Fig. 1. Evaluation of burning velocity data for the pyrotechnic mixtures: line a, 7%B-93%MoO_3; line b, 50% W-50%$K_2Cr_2O_7$; line c, 5%B-95%$K_2Cr_2O_7$.

where E_{app} is the apparent activation energy derived from the gradient. We have measured the exothermicity and heat capacity of the present mixtures by calorimetry and estimated ΔT_{ad}, from which T_m has been calculated via $T_m = T_a + \Delta T_{ad}$ where T_a is the initial temperature. The assumption has been made that ΔT_{ad} is a constant for each pyrotechnic mixture and is independent of the initial temperature.

Our results are shown in Fig. 1 from which it is apparent that the data may reasonably be represented by straight lines. Considerable care was taken to obtain precise burning velocities: each value was the mean of at least five measurements with a standard deviation of 2–5%. Table 1 shows both the "apparent" and "true" activation energies for the three pyrotechnic mixtures. The effect of the high mean values of T_m is to reduce the value of the apparent activation energy by about a half. Indeed, the values are too low for the validity of the Zel' dovich and Frank-Kamenetskii approach to

TABLE 1

Kinetic parameters for the three pyrotechnic mixtures

Pyrotechnic mixture	ΔT_{ad} (K)	E_{app} (kJ mol^{-1})	E (kJ mol^{-1})	ln A (s^{-1})
50%W-50%$K_2Cr_2O_7$	1640	109±6	42±6	8.9±0.7
5%B-95%$K_2Cr_2O_7$	1540	111±6	47±6	10.1±0.6
7%B-93%MoO_3	2300	104±7	27±7	6.7±0.7

the calculation of burning velocity. Computed exact solutions of the propagation equation indicate that for the values of $E/R\bar{T}_m$ in the present work (1.5–3.5) the error introduced in the burning velocity is 30%–40%. However, this error does not change markedly over the present rather restricted range of T_m, which lends credence to the activation energies derived. The pre-exponential factor A has been estimated from eqn. (1). We have assumed a thermal diffusivity of 1.5×10^{-7} m^2 s^{-1} for the mixtures, but in view of the inadequacy of the model the reliability of the results is doubtful; values of ln A (s^{-1}) may involve a systematic error of ± 0.5.

The activation energy of very few gasless pyrotechnics has been determined. This is in spite of the importance of activation energies in modelling combustion phenomena in pyrotechnic systems. There are only a small number of experimental techniques which find application and the results are often contentious. The analysis of temperature profiles invariably gives very low activation energies: for 50% tungsten–50% potassium dichromate the value $E = 11$ kJ mol^{-1} has been obtained. The technique is not straightforward and involves many assumptions not easily tested. Part of the reason for the present work was to examine an alternative technique, far simpler, but still concerned directly with the propagation process. Perhaps the most obvious feature of the present results is the activation energies which are low (less than 50 kJ mol^{-1}) compared with those reported from non-ignition studies by thermal analysis [4–7]. This emphasizes the need for caution when ascribing activation energies to the combustion process when they have been obtained from studies where a different rate-determining step may prevail.

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