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Experimental Studies of the Propagation of Combustion in Solids [and Discussion]

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Experimental studies of the propagation of combustion in solids

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The application of thermal methods to the study of steady-state combustion is described. Such methods provide a route to information on heat transfer and chemical kinetics which forms a basis for the implementation of numerical models. The experimental results from thermal analysis and temperature profile analysis have been examined within the context of a simple pseudo one-dimensional model of propagation offering some confirmation of the validity of the approach.

1. Introduction

The combustion of solids represents a major area of science and technology. In this paper the concern has been narrowed down to the self-sustained steady-state propagation in all-solid régimes: the basis of practical pyrotechnic delays. Here interest lies in the mechanism of propagation and the related problem of predicting the burning velocity. As a source of recurring interest it brings together practical requirements and aspects of more fundamental research. Considerable advances have been made in our understanding of the factors that influence combustion. Even so the development of practical delays with reproducible functioning times remains largely due to the skill of the practitioner.

Our understanding of steady-state combustion has been considerably enhanced through the application of thermal techniques. These can be traced to the foundation of modern research: the papers by Spice & Stavely (1949*a*, *b*) led to the identification of a pre-ignition reaction and a classification of pyrotechnics according to their stoichiometry; those by Hill *et al.* (1950) and Hill (1954) linked the kinetics of the chemical reaction to the temperature–time history measured through the combustion wave. The use of thermal analysis was firmly established in the 1950s with the early work from Picatinny Arsenal (Gordon & Campbell 1955). Since then thermal analysis has evolved as a key technique in the investigation of the chemistry of pyrotechnic systems.

Temperature profile analysis

This term has been coined to describe the measurement and interpretation of the temperature–time history through the combustion wave. The technique provides a route to information on heat transfer and reaction kinetics, difficult if not impossible to obtain by other techniques. The important quantities that can be derived include the adiabatic temperature change and the instantaneous rate of heat evolution and thence to a description of the reaction kinetics. Even so there were few developments in either instrumentation or interpretation of results after the work of Hill *et al.* until thirty years later when Boddington *et al.* (1982*a*) elaborated the theory in more detail. Hill *et al.* were the first to pinpoint activation energies which seemed to be

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unusually low but which were consistent with the weak temperature dependence of the burning velocity. In direct contrast are the results from thermal analysis where the activation energies are an order of magnitude greater.

Thermal analysis

This is a generic term describing a number of techniques but in the present context it refers to differential thermal analysis (DTA) and differential scanning calorimetry (DSC). These two techniques are concerned with the measurement of energy changes and are universal in their application to pyrotechnics. More restricted in its application is thermogravimetry where the concern is with mass changes. DTA and DSC experiments under conditions which lead to ignition of the sample show a sharp exotherm in the thermal analysis curve. Analysis is limited to the identification of ignition temperatures but has led to a general exploration of the effect of composition on ignition characteristics. A recent development has been to model the response of the thermal analyser to the ignition process (Erickson *et al.* 1986, 1987). Under non-ignition conditions where the thermal analysis curve shows a series of peaks corresponding to the reaction stages the primary aim is to identify those stages. There is a dependence on complementary techniques, most notably X-ray diffraction but also spectroscopy, microscopy and evolved gas analysis. This last technique as applied to gassy pyrotechnics forms a direct parallel to the use of X-ray diffraction studies of solids.

2. Experimental and discussion

Our aim was two-fold: to propose a mathematical model of the propagation process and to extend the scope of thermal analysis as applied to pyrotechnics. Simplicity of concept and ease of implementation were determining features in the derivation of the model (Boddington *et al.* 1989). The mathematical approach has much in common with that of earlier authors (Shkadinskii 1971; Shkadinskii *et al.* 1971; Strunina *et al.* 1974, 1981; Ivleva *et al.* 1983). We were particularly concerned to link the model with the ability to furnish realistic values of the input parameters having regard for the dearth of information on the kinetic and thermal properties of pyrotechnic systems. A pseudo one-dimensional approach has been adopted in which an allowance for heat loss has been made by a simple newtonian heat transfer term.

The key equation is

$$\sigma c \frac{\mathrm{d}T}{\mathrm{d}t} = \kappa \frac{\mathrm{d}^2 T}{\mathrm{d}z^2} - h(T - T_\mathrm{a}) + w, \tag{1}$$

which expresses the heat balance across a section of pyrotechnic normal to the axis of propagation. T is the mean temperature and z the axial coordinate; σ, c and κ denote the density, specific heat capacity and thermal conductivity respectively; w is the rate of heat evolution due to chemical reaction per unit volume and $h(T-T_\mathrm{a})$ represents lateral heat loss, where h is the heat loss coefficient. T_a is the ambient temperature. The model ignores mass flow and is applicable in its entirety to gasless pyrotechnics only.

Our early experimental work was carried out with pyrotechnic mixtures of tungsten and potassium dichromate. These have the merit of burning smoothly over a wide range of compositions with almost no change in weight (less than 1%). Thermal analysis (Charsley *et al.* 1978) indicated ignition at about the melting

Table 1. *Burning velocity v and exothermicity Q for mixtures of tungsten and potassium dichromate (Boddington et al. 1982a)*

	tungsten (%)						mean errors (%)
	30	40	50	60	70	80	
v (measured)/(mm s^{-1})	1.43	8.0	14.4	19.7	25.2	18.8	3
v (calculated)/(mm s^{-1})	1.01	7.2	12.1	16.2	24.3	14.4	20
Q (measured)/(kJ g^{-1})	0.93	1.11	1.08	0.94	0.71	0.56	4
Q (calculated)/(kJ g^{-1})	1.10	1.40	1.20	1.00	0.75	0.50	10

temperature of potassium dichromate (671 K) and a two stage reaction in which potassium dichromate is converted to potassium chromate and subsequently chromic oxide (Cr_2O_3). However, the relevance of thermal analysis experiments to propagation is not assured bearing in mind the very different rates of temperature rise, typically 10 K min^{-1} in thermal analysis as compared with 10^5 K min^{-1} in combustion.

The validity of equation (1) is crucial to our approach. It is inherently plausible but the quantitative verification is by no means straightforward. The equation can be recast in a form which allows the burning velocity and exothermicity to be derived from measurements of the temperature profile. These values may then be compared with the results from independent measurements. The temperature profile measurements were carried out using thermocouples pressed into the pyrotechnic mixture which was contained in channels made of a variety of materials. The thermocouple signals were recorded using a microprocessor on-line to a VAX computer used for the subsequent numerical processing. Burning velocities were obtained by measuring the time taken for the combustion wave to propagate over a known distance. The exothermicity of the combustion reaction was measured by burning samples in an adiabatic combustion calorimeter.

The results are shown in table 1. They appear to confirm the validity of the approach albeit within large errors. Caution is needed in assessing the results since the analysis can only proceed on the basis of a number of assumptions. These include the temperature independence of heat capacity and thermal conductivity although in practice no other assumption could be made since we have so little experimental information. The calculation of the burning velocity draws attention to the thermal diffusivity ($\kappa/\sigma c$), another parameter for which we have only limited information in the context of pyrotechnics. We have modified commercial thermal analysis equipment to meet this deficiency but the measurements are at temperatures far removed from those in the combustion wave (Boddington *et al.* 1982*b*, 1983).

The full potential of temperature profile analysis is revealed when used to derive the heat transfer terms (Boddington *et al.* 1986). It is possible to map out the dependence of lateral heat loss on the cross-sectional area of the pyrotechnic column together with the nature of its container and in this way to begin to offer some criteria for failure of combustion. In our approach to kinetics we have assumed a rate law with an Arrhenius temperature dependence. The latter allows us to compare our results with those published by Hill *et al.* The approach is iterative: different rate laws are assumed and the calculated rates of heat evolution are compared with that derived from the temperature profile. Values for the pre-exponential factor and activation energy derived in this way are shown in table 2. They are based on a

Table 2. *Pre-exponential factor A and activation energy E for the combustion of tungsten and potassium dichromate measured by temperature profile analysis (Boddington et al. 1986)*

	tungsten (%)						mean
	30	40	50	60	70	80	errors (%)
$10^{-2}\ A/\mathrm{s}^{-1}$	0.5	2.9	5.8	9.2	12.7	6.8	50
$E/(\mathrm{kJ\ mol}^{-1})$	15.1	10.9	12.3	10.5	11.0	9.6	25

Table 3. *Comparison between measured burning velocities and the values derived from the numerical model*

composition	burning velocity, $v/(\mathrm{mm\ s}^{-1})$ measured[a]	calculated[b]
37.5% W–37.5% $K_2Cr_2O_7$–25% $BaCrO_4$	2.40	2.08
11% B–89% MoO_3	7.40	8.96
47.5% W–47.5% $K_2Cr_2O_7$–5% Cr_2O_3	4.29	5.95
45% W–45% $K_2Cr_2O_7$–10% Cr_2O_3	3.41	5.50
42.5% W–42.5% $K_2Cr_2O_7$–15% Cr_2O_3	2.69	5.06

Mean error: [a] 7%, [b] 15%.

simple nth order isothermal rate law: more complex laws did not provide a better fit with the experimental data. Once again the reliability of the results is open to question in view of the assumptions made in the analysis. Furthermore the analysis depends not only on the temperature profile itself but also on the first and second derivatives with respect to time. It these are not to swing violently in magnitude and sign it is necessary that the raw experimental data be smoothed but not at the expense of relevant detail. The low activation energies are the obvious feature of the results, a similar outcome obtained by Beck & Brown (1985) for mixtures of antimony and potassium permanganate.

Following the measurement of the thermal and kinetic parameters we may return to the model of combustion to seek numerical solutions of equation (1). Initially we obtain the progress of the temperature wave through the pyrotechnic and from this we derive the burning velocity. In table 3 a comparison is made between the calculated burning velocities and those measured for a range of compositions. This comparison suggests that the model is able to reproduce the trends in burning velocity. The uncertainties in the calculated values are large and the close agreement sometimes observed between calculated and experimental results is probably fortuitous. It is possible to explore the complex interrelationships between burning velocity, heat loss and activation energy although the practitioner has little control over the activation energy. With large activation energies the model suggests the rapid onset of combustion failure. It may be argued that the work is a test of consistency since both the model and temperature profile analysis are based ultimately on the same equation. However, it is possible to extend the model to problems outside the immediate range of experiments. In any event it provides a framework against which the mass of empirical information may be judged.

The role of kinetics derived from thermal analysis still remains unresolved. Table 4 lists activation energies derived from thermal analysis and temperature profile analysis. The dependence of the values on the technique used for their measurement

Table 4. *Activation energies E from thermal analysis* (TA) *and temperature profile analysis* (TPA)

composition	$E/(\text{kJ mol}^{-1})$	
Zr–MoO_3	272	TA (Beardell & Kirshenbaum 1974)
B–KNO_3	286	TA (Whelan *et al.* 1985)
B–Pb_3O_4	434	TA (Whelan *et al.* 1986)
Fe–$KMnO_4$	25–65	TPA (Hill 1954)
Sb–$KMnO_4$	20–24	TPA (Beck & Brown 1985)
B–MoO_3	13	TPA
W–$K_2Cr_2O_7$–$BaCrO_4$	23	TPA
W–$K_2Cr_2O_7$	12	TPA (Boddington *et al.* 1986)

Table 5. *Pre-exponential factor A and activation energy E for the reaction between tungsten and potassium dichromate measured by differential thermal analysis*

potassium dichromate	$E/(\text{kJ mol}^{-1})$	$\ln (A/\text{s}^{-1})$	fractional extent of reaction
molten	235 ± 11	37 ± 2	0.5
	243 ± 15	39 ± 1	0.7
	239 ± 8	36 ± 3	0.9
solid	219 ± 19	31 ± 4	0.2–0.8

is self-evident. An obvious omission is a single pyrotechnic system investigated by both techniques. We have used thermal analysis to study those mixtures of tungsten and potassium dichromate used in the temperature profile analysis. Once again we have assumed the same form of kinetic law, merely for the purposes of comparison. The results are shown in table 5. They are a representation of the empirical data but carry no mechanistic implication. Our proposal is that the rapid temperature rise in the initial stage of the combustion wave is controlled by those very kinetic parameters identified by thermal analysis. The use of a more complex rate law incorporating the results from both temperature profile analysis and thermal analysis allows us to extend the model to explore problems of transient behaviour (Boddington *et al.* 1990). These are exemplified by combustion transfer from one pyrotechnic to another either directly or through an inert septum, problems with practical implications.

The central role of thermal analysis in the study of pyrotechnic combustion is evidenced by the number of papers which have been published dealing with the many aspects of this subject area. The most recent review is that of Laye & Charsley (1987). Frequently recurring themes for study are multistage reactions; the relation between surface and bulk phase reactions; the relevance of phase transitions to onset temperatures. The wide ranging applications have been facilitated by the variety of commercial equipment readily available. Much less prolific have been publications based on the use of temperature profile analysis. The reasons are not difficult to comprehend. The measurements are not straightforward and furthermore it is necessary to correct the thermocouple signal for perturbation introduced by the thermocouple itself. Overall there seem to be few pyrotechnic systems that burn sufficiently smoothly without the evolution of gas to allow measurements to be made. At first sight pyrometry appears to offer some advantages over the use of thermocouples but in practice problems arise in attempting to correct for the response characteristics of the associated equipment. Both thermal analysis and temperature profile analysis are 'macroscopic' techniques and information on the mechanism at the microscopic level can only be obtained by inference. For such information on gasless systems we must turn to innovative research where surface spectroscopic techniques have been used to probe mechanisms (Erikson *et al*. 1986, 1987). The results have offered a solution to the inverse problem of predicting the shape of thermal analysis curves. For gassy systems we already have the well established use of optical spectroscopy. The future seems set for the continuing use of a wide range of different techniques in the study of pyrotechnic combustion. Even so our ability to provide the necessary thermokinetic information is likely to remain the limiting factor in the use of models.

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Discussion

C. P. Constantinou (*Cavendish Laboratory, Cambridge, U.K.*). You have stated that a first-order kinetic function will fit the decomposition rate measurements as well as any other and so have presumably made this assumption in determining the pre-exponential factor. The assumption essentially amounts to fitting a sigmoid shaped curve with a function that varies with reduced time proportionally to $1-e^{kt}$. I would therefore agree that the values for the activation energy and especially the pre-exponential factor that you have quoted do not bear any relation to fundamental microscopic parameters. T. B. Tang and M. M. Chaudhri (*J. thermal Analysis* **17**, 359–370 (1979)) have discussed the influence of physical mechanisms, like diffusion and power law nucleation for example, on the kinetic function, and have stressed the importance of judging the consistency of activation energies and reaction rate constants with possible reaction mechanisms. In view of this, it should be possible by choosing a plausible kinetic function to arrive at physically meaningful kinetic parameters.

P. G. Laye. I agree with the comment. The single aim of the present investigation was to obtain an expression that represented as closely as possible the rate of reaction. A first-order isothermal law was used since other rate laws did not give a significantly better fit to the experimental data. However, to represent the results by a rate law that might be regarded as more plausible without an improved fit would be to deny the validity of the experimental data.

F. Volk (*Fraunhofer Institute, F.R.G.*). A very low activation energy of black powder is quoted, but a very high value for B-KNO_3. Both igniters contain potassium nitrate as an oxidizer. What could be the reason for the low value of black powder? Could it be sulphur?

P. G. Laye. As might be expected, the kinetic results for black powder are confusing with a wide range of activation energies depending on the precise nature of the sample. C. Campbell and G. Weingarten (*Trans. Faraday Soc.* **55**, 2221–2228 (1959)) found the key reaction to be between sulphur and potassium nitrate and obtained an activation energy of 56.9 kJ mol^{-1} from ‘time to ignition’ measurements. A. D. Kirshenbaum (*Thermochim. Acta.* **18**, 113–123 (1977)) obtained much higher activation energies from thermal analysis experiments but confirmed that the presence of sulphur reduces the activation energy.