

## Note

**DIFFERENTIAL THERMAL ANALYSIS AND TEMPERATURE PROFILE ANALYSIS OF PYROTECHNIC SYSTEMS: MIXTURES OF IRON AND POTASSIUM DICHROMATE**

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The pyrotechnic reaction between iron and potassium dichromate has been studied by Hill et al. [1] and more recently by Rees [2]. The gasless nature of the reaction and the low burning temperature make the measurement of temperature profiles deceptively easy. Our measurements on mixtures containing 50, 60 and 70% \* iron indicate considerable variation even between temperature profiles recorded for the same mixture. The temperature profiles were recorded using a thermocouple embedded in an open-train of the pyrotechnic mixture [3]. With fine iron powder (mean particle diameter  $<10 \mu\text{m}$ ) the mixtures were difficult to ignite and when pressed failed to propagate a combustion wave. Mössbauer spectroscopy showed that the iron was free from surface oxide. The experimental results are shown in Table 1. The errors are the standard deviation of the means, and for the exothermicity they include an uncertainty of  $\pm 25\%$  in the estimated effective heat capacity.

The temperature profiles may be analysed to give the instantaneous rate of evolution of heat (power) from which the chemical kinetics may be derived [3]. We have assumed that the rate of reaction may be represented by the equation

$$d\epsilon/dt = A(1 - \epsilon)^n \exp(-E/RT)$$

where  $\epsilon$  is the fractional extent of reaction;  $n$  is the order of the reaction; and  $E$  is the activation energy. Values of  $n$  and  $E$  have been estimated using an iterative least squares procedure in which the experimental chemical power is compared with that calculated on the basis of the above rate equation. Figs. 1 and 2 show a comparison between the experimental and calculated power functions for two mixtures. The mean results from six analyses are  $n = 1.2 \pm 0.3$  and  $E = 92 \pm 14 \text{ kJ mole}^{-1}$ . Some power functions showed a small incompletely resolved high temperature exotherm which has been excluded from the kinetic analysis. There are also differences between the

\* In expressing compositions, % =  $100 \times$  weight of the component/weight of the mixture.

TABLE 1

## Combustion results

% Iron	Burning velocity (mm s <sup>-1</sup> )	Max. temp. (K)	Exothermicity <sup>a</sup> (J g <sup>-1</sup> )
50	0.86 ± 0.02	1086 ± 19	890 ± 240
60	0.50 ± 0.01	998 ± 52	740 ± 190
70	0.35 ± 0.01	916 ± 34	660 ± 170

<sup>a</sup> Values have been derived from the temperature profiles and refer to 1 g of mixture.

curves obtained by differential thermal analysis under non-ignition conditions. The main exotherm is broad and poorly defined. With samples weighing 20 mg and using a heating rate of 10 K min<sup>-1</sup>, the exotherm becomes pronounced at 800 K, but with larger samples and faster heating rates it is established immediately following the fusion endotherm of potassium dichromate (~670 K). The present value of the activation energy is considerably greater than that reported by Hill et al. [1] for pressed mixtures. A similar discrepancy was observed between high and low density mixtures of iron and potassium permanganate where the higher activation energy was identified with the decomposition of the oxidant [4]. A complete account of the kinetic analysis will be published later.

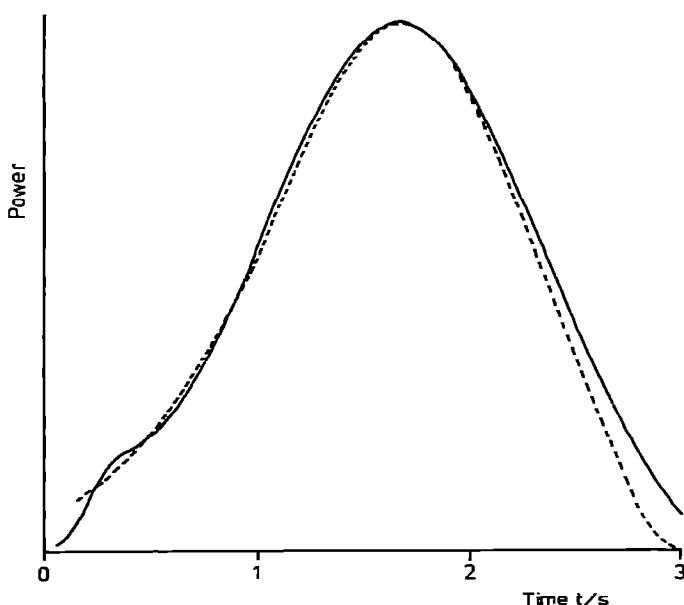


Fig. 1. Comparison between experimental and calculated power functions for a mixture containing 50% iron. —, Experimental curve; - - - -, calculated curve.

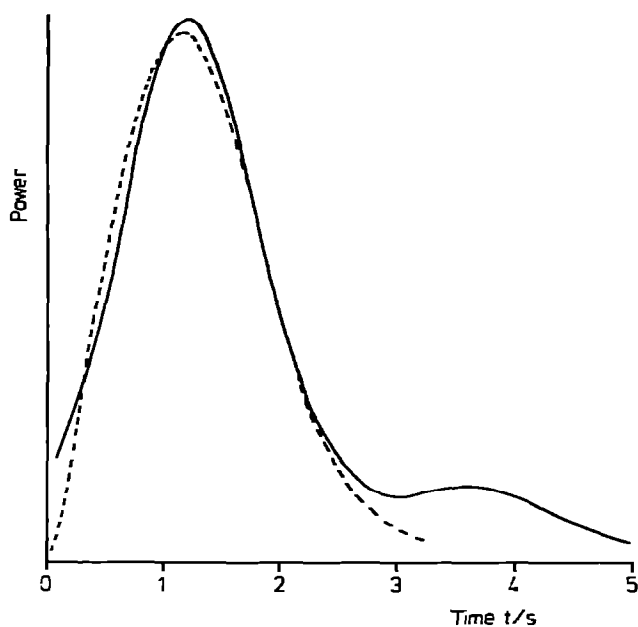


Fig. 2. Comparison between experimental and calculated power functions for a mixture containing 60% iron. —, Experimental curve, - - - - - , calculated curve.

#### REFERENCES

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