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Reaction kinetics of mixtures of tungsten and potassium dichromate

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Abstract

The kinetics of the reaction of tungsten and potassium dichromate has been studied by thermal analysis. The activation energy is an order of magnitude greater than that determined by combustion studies. The present results may describe the low-temperature behaviour which is the precursor to steady-state combustion.

INTRODUCTION

Mixtures of tungsten and potassium dichromate are typical of gas-less pyrotechnic delay compositions in which the self-sustained combustion wave is accompanied by a minimal evolution of gas (< 1 cm^3 g^{-1} of mixture). Our earlier analysis of the temperature–time history through the combustion wave yielded a formal description of the rate of the combustion reaction [1]. In contrast, the kinetics of the reaction under non-ignition conditions has formed the focus of attention in the present investigation. Studies of other pyrotechnic systems [2–7] have yielded high activation energies (100–300 kJ mol^{-1}). However such values are inconsistent with the derivation of steady-state burning velocities using simple numerical models [8,9]. Combustion studies [1,10–15] yield low activation energies (10–70 kJ mol^{-1}) and although these lead to a description of the properties of steady-state combustion they give rise to erroneous predictions of the transient behaviour in combustion transfer and pick-up. It is these apparent inconsistencies in the limited kinetic information available which has prompted this investigation. The objective is a comparison of the kinetic parameters for the same pyrotechnic mixture determined under both ignition and non-ignition conditions.

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EXPERIMENTAL

A mixture containing 50% (weight of component × 100/weight of mixture) tungsten (particle size 0.8 μm) and 50% potassium dichromate was prepared by sieve-mixing the weighed components [16]. The mixture corresponded to that used in the earlier work and contained the original samples of tungsten and potassium dichromate.

Thermal analysis (differential scanning calorimetry and differential thermal analysis) has been used to determine both the rate and extent of reaction. Calibration of the apparatus links the instrument signal S to the differential thermal power $\mathrm{d}\Delta q/\mathrm{d}t$ from which the rate of reaction may be calculated, $\mathrm{d}\alpha/\mathrm{d}t = (\mathrm{d}\Delta q/\mathrm{d}t)/\Delta H$ where α is the fractional extent of reaction and ΔH is the enthalpy of the reaction. We have expressed the rate of reaction as separable functions of the extent of reaction and temperature $\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)g(T)$. In common with other authors we have assumed that the temperature dependence is represented by an Arrhenius expression, $g(T) = A\,\exp(-E_\mathrm{a}/RT)$ where A and E_a are the pre-exponential factor and activation energy respectively. In dynamic experiments allowance must be made for the contribution of the instantaneous heat capacity of the reactants and products to the instrument signal in calculating the thermal power and enthalpy associated with the reaction. The assumption has been made that there is a direct proportionality between the extent of reaction and the enthalpy change for the isothermal reaction.

The equipment (Perkin–Elmer, DSC model 4 and Stanton Redcroft Thermal Analyser, model STA 781) was calibrated using conventional chemical standards. The pyrotechnic mixture was studied in both isothermal and dynamic experiments. The samples were contained in platinum crucibles with loose-fitting lids. Typical sample masses were 5 mg. An atmosphere of argon was maintained in the apparatus to prevent aerial oxidation of the tungsten. The reference was an empty crucible.

In the dynamic experiments the pyrotechnic mixture was heated from 635 to 725 K at 5 K min^{-1}. The heat capacity of the reactants was measured in separate experiments. The difference between the heat capacity of solid and molten potassium dichromate has been reported [17]. The heat capacity of the products was estimated by recording the thermal analysis curve over the same temperature range (635–725 K) used in the original experiment. The enthalpy of fusion of potassium dichromate has been reported [17] and the enthalpy change could be calculated for the isothermal reaction between tungsten and both solid and molten potassium dichromate.

In the isothermal experiments the samples were heated to 623 K and, once the instrument signal had stabilised, heated rapidly (150 K min^{-1}) to the working temperature (665–695 K). The thermal analysis curves were recorded until the reaction was complete; no further exotherms were observed when the products were heated to 725 K. Experiments at temperatures below 665 K gave very small instrument signals and reaction times which could extend over several days. This was inconveniently long for conventional thermal analysis experiments. An alternative procedure was adopted in which samples of the pyrotechnic mixture were sealed into glass tubes under vacuum and placed in an oven with a precisely controlled temperature for varying times (45 min to 90 h). The extent of reaction was obtained by comparing the enthalpy derived from a subsequent dynamic experiment in which the residue was heated to 800 K, with the enthalpy for complete reaction, both corrected to the temperature of the isothermal experiment.

RESULTS AND DISCUSSION

The thermal analysis curves recorded under dynamic conditions showed the expected broad exotherm starting at about the melting temperature of potassium dichromate (671 K). The reaction has been identified as $W + 2K_2Cr_2O_7 = WO_3 + 2K_2CrO_4 + Cr_2O_3$ (24.5 mass% tungsten) [18]. The shape of the early portion of the peak is affected by the melting of the potassium dichromate making it difficult to obtain reliable kinetic information from the dynamic experiments. A small exotherm immediately leading to the fusion endotherm may represent a 'true' solid-state reaction. However, the presence of localised pockets of molten potassium dichromate cannot be ruled out: the melting temperature of potassium dichromate can be depressed 10 K by the presence of reaction products.

The thermal analysis curves from the isothermal experiments (695–710 K) showed only a decay following the initial period during which isothermal conditions were established. Plots of ln S against time ($S \propto$ rate of reaction) in a test for simple first-order kinetics gave straight lines (correlation coefficient $\geqslant 0.98$). Figure 1 shows the results for one such experiment where the straight line (correlation coefficient = 0.996) extends over the range $\alpha = 0.4$–0.9. Thus for a major part of the reaction regime the rate may be described adequately by a first-order rate law. It does not apply over the range $\alpha = 0.3$–0.4 where the observed reaction rate is much greater than that expected on the basis of the law. We have examined the application of other rate laws but no single law gave an improved description of the results over a more extensive portion of the reaction. An investigation of the early portion of the reaction, $\alpha \leqslant 0.3$, was precluded by the lack of a meaningful signal.

The Arrhenius parameters have been obtained independently of the isothermal rate law from the temperature dependence of the rate of reaction at fixed extents of reaction. The fractional extents of reaction were calculated from the partial area enclosed by the thermal analysis curves (working backwards from the end of the reaction) and the area expected

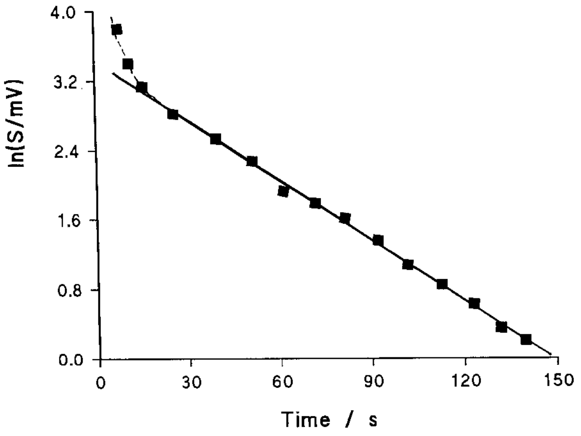

Fig. 1. Test for simple first-order kinetics for the reaction between tungsten and molten potassium dichromate.

for the complete reaction. The values obtained for the activation energy and pre-exponential factor are summarised in Table 1. The errors can be traced to difficulty in defining the fractional extents of reaction. We have included an allowance for uncertainty in the area to be assigned for complete reaction. Within the errors the kinetic parameters are constant over the range $\alpha = 0.5$–0.9 which supports the proposition for a fixed mechanism in the same regime as that identified with the first-order rate law. The Arrhenius parameters obtained from the temperature dependence of the first-order rate constant were $E_a = 234 \pm 11$ kJ mol^{-1} and ln A (s^{-1}) $= 37 \pm 2$. Measurements have also been made with mixtures containing tungsten with a particle size of 0.5 μm. The mean kinetic parameters were $E_a = 239 \pm 15$ kJ mol^{-1} and ln A (s^{-1}) $= 40 \pm 2$ from which it seems that the effect of particle size is most evident in the magnitude of the pre-exponential factor.

The much reduced rate of reaction observed in the preliminary thermal analysis experiments at temperatures below 665 K was taken to indicate a solid-state reaction between tungsten and potassium dichromate. The appearance of the residue was different from that obtained at higher temperatures and showed no signs of the presence of a molten phase during the

TABLE 1

Kinetic parameters for the reaction of tungsten with molten potassium dichromate

E_a (kJ mol^{-1})	ln A (s^{-1})	α
235 ± 11	37 ± 2	0.5
243 ± 15	39 ± 1	0.7
239 ± 8	36 ± 3	0.9

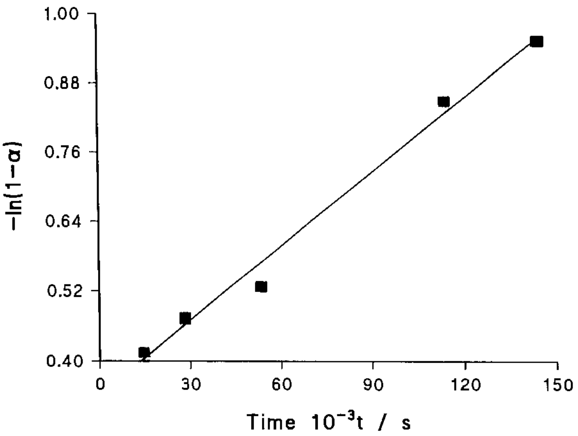

Fig. 2. Test for simple first-order kinetics for the reaction between tungsten and solid potassium dichromate at 625 K.

reaction. The technique adopted in which the samples were heated in an oven led to information about the extent of reaction as a function of time at a series of temperatures (620–660 K). We find that within the experimental error our data may be represented by a first-order rate law. Depending on the temperature and time, this extended over the range $\alpha = 0.2$–0.8. The results shown in Fig. 2 ($\alpha \approx 0.3$–0.6) are for measurements over 41 h at 625 K. The kinetic parameters are given in Table 2. The values show that the much slower rate of reaction observed with solid potassium dichromate is associated predominantly with the smaller pre-exponential factor. The shape of the exotherms obtained in the dynamic experiments on the residues was considerably broader than that with fresh mixtures. This was particularly so for those mixtures where extensive reaction had taken place in the solid-state and the presence of products inhibited further reaction. Area measurements were made on exotherms resolved using the high-temperature thermal analyser. We have also calculated rate data as a function of time to derive the Arrhenius parameters independently of the isothermal rate law. Large uncertainties arise in the calculations but the results obtained offer confirmation of the values derived from the temperature dependence of rate constants obtained from the first-order plots.

TABLE 2

Kinetic parameters for the reaction of tungsten with solid potassium dichromate

E_a (kJ mol^{-1})	ln A (s^{-1})	α
219 ± 19	31 ± 4	0.2–0.8
242 ± 38	29 ± 6	0.4
229 ± 33	27 ± 5	0.6

SUMMARY

The present investigation allows a comparison between the kinetic parameters for the same pyrotechnic mixture measured under ignition and non-ignition conditions. The comparison highlights the quite different results which have been obtained. It points to a dependence of the kinetic results on the temperature–time history to which the sample is subjected in the experimental technique. More generally it provides a rationalisation of the disparate results which have been reported based on different experimental techniques. For mixtures of tungsten and potassium dichromate, the melting of the oxidant influences strongly the shape of the thermal analysis curves. At about the melting temperature of potassium dichromate, the rate of reaction of tungsten with molten potassium dichromate is about an order of magnitude greater than that for the reaction with solid potassium dichromate. The present kinetic results are to be regarded as a convenient description of the empirical data with no implication concerning the mechanism of the reaction.

The activation energies determined in the present work are an order of magnitude larger than that obtained previously from combustion studies. They would lead to a temperature dependence for the burning velocity far greater than would be acceptable for a conventional pyrotechnic delay composition. The apparent dependence of the results on the temperature–time history of the sample raises the question of how far a simple Arrhenius temperature dependence can adequately describe the rate of reaction during both combustion pick-up and steady-state combustion. We argued previously [9] that the low-temperature behaviour might be represented by an Arrhenius-like term which describes a rapid increase in the rate of reaction as the temperature rises. We now propose that the results from thermal analysis constitute this term which dominates the reaction kinetics at low temperatures. At high temperatures the propagative behaviour is determined by a 'diffusion' term with only a feeble temperature dependence which accounts for the small temperature dependence of the burning rate.

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