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THERMAL RUNAWAY BY THERMAL ANALYSIS

T. BODDINGTON, FENG HONGTU, P.G. LAYE, M. NAWAZ
and DOROTHY C. NELSON

School of Chemistry, The University, Leeds LS2 9JT (Gt. Britain)

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ABSTRACT

The effect of heating rate on thermal runaway has been investigated by thermal analysis. For the materials studied in the present work there was an increase in the ignition temperature as the heating rate was increased. At high heating rates the effect was largely determined by the thermal relaxation time. A simple analytical model of the experiment accounted for the trend in the results but led to unacceptable values for the thermokinetic parameters of the system.

INTRODUCTION

The facility with which dynamic experiments can be carried out provides the rationale for the extensive use of thermal analysis to obtain kinetic parameters. Not least amongst the assumptions made is that the temperature of the sample is uniform and that it changes linearly with time. These assumptions form the focus of the present work. With large sample masses and high heating rates temperature excesses may be established which may lead to thermal runaway and ignition. Nowhere is this more important than with the use of heating rate as an independent variable in the investigation of kinetics. The methods discussed, notably by Kissinger [1,2] and Ozawa [3,4], fall within this description and form the basis of the ASTM test method E698 for the determination of the kinetic constants of hazardous materials. An account of the influence of self-heating on the determination of reaction rate from thermal analysis curves has been given by Merzhanov et al. [5]. We have investigated the effect of heating rate on thermal runaway for three energetic materials, one an explosive, and the other two pyrotechnics. Interpretation of the results has been guided by simple ignition theory.

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EXPERIMENTAL

Materials

Explosive

This contained 46% ethylenediaminedinitrate, 46% ammonium nitrate and 8% potassium nitrate (all percentages by weight).

Pyrotechnics

These were mixtures of 5% boron with 95% barium chromate and 50% tungsten with 50% potassium nitrate. The boron was amorphous grade and the mixtures were prepared by brush mixing the weighed components through a fine seive (200 mesh, 75 μm).

Thermal analysis

Experiments were carried out using differential scanning calorimetry (Perkin–Elmer DSC 4) and differential thermal analysis (Stanton Redcroft simultaneous DTA–TG, model 781). The DTA was calibrated to give an instrument signal proportional to thermal power [6]. Temperature calibration for both instruments was obtained by assigning the fusion temperature of metals (indium, tin and lead) to the extrapolated onset temperature of the recorded fusion peak. The calibration was carried out over the range of heating rates used in the subsequent experiments.

The explosive was studied in both the DSC and the DTA equipment. Samples were contained in aluminium crucibles closed by a lid with a small hole (diameter 0.5 mm). The pyrotechnic mixtures were studied in the DTA apparatus. Platinum crucibles were used for the tungsten mixture and quartz crucibles for the boron mixture where there is a risk of platinum being corroded at high temperatures. The experiments were carried out with an atmosphere of flowing argon in the apparatus. The heating rates were measured from the temperature–time curves.

RESULTS AND DISCUSSION

The three materials showed a similarity in their underlying trend towards self-heating and ignition. With small sample masses and slow heating rates the temperature rises observed by DTA were modest (< 0.1 K). For larger masses and more rapid heating the temperature rises were large, often exceeding 100 K. The rate of temperature increase exceeded the programmed heating rate, leading to a sharp ignition peak and a "spike" on the temperature–time curve. The distinction between non-ignition and ignition is exemplified by the thermal analysis curves shown in Fig. 1 for the

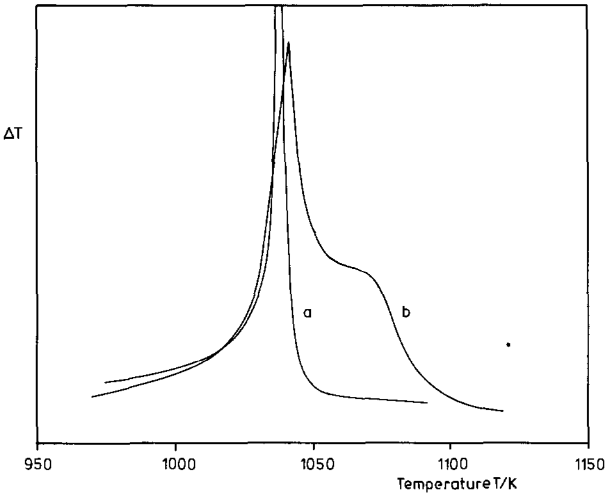

Fig. 1. The DTA curves obtained for a mixture of 5% boron and 95% barium chromate under (a) ignition and (b) non-ignition conditions.

pyrotechnic mixture containing boron and barium chromate. With power-compensated DSC the temperature signal is derived from the programmer and the temperature evolution is not observed. Figure 2 shows the ignition results obtained by DTA. The temperature of ignition, (T_{ign}) was identified with the extrapolated onset temperature of the peak. The present materials all showed an increase in the ignition temperature as the heating rate was

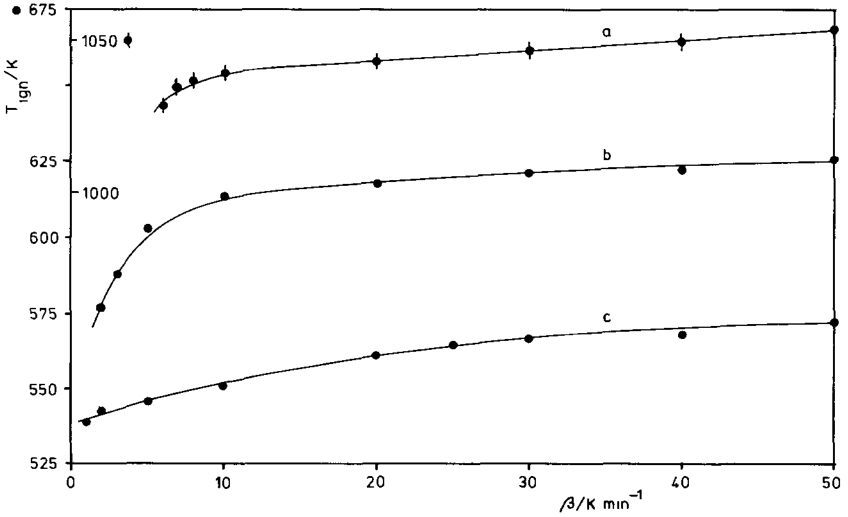

Fig. 2. Ignition results for (a) 5% boron–95% barium chromate, (b) 50% tungsten–50% potassium nitrate and (c) explosive.

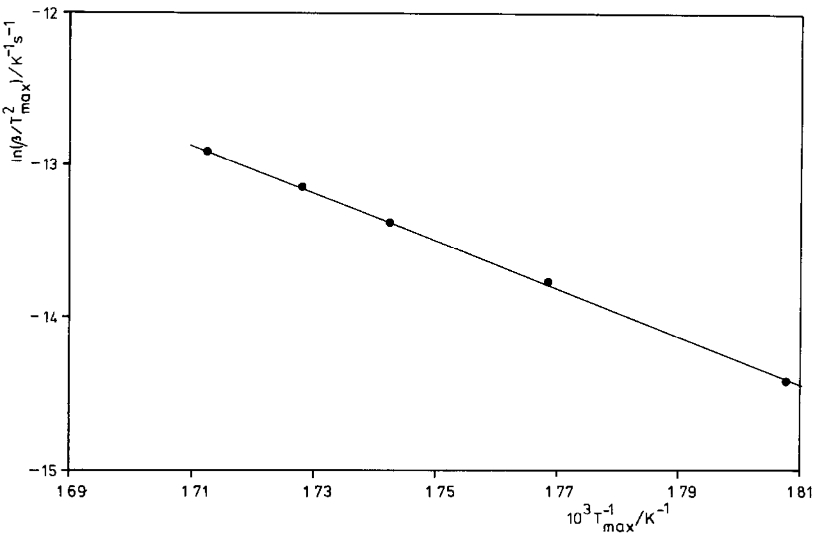

Fig. 3. Determination of the activation energy of the explosive from DSC experiments under non-ignition conditions.

increased. This pattern of behaviour is not universal: results published for a mixture of magnesium–barium peroxide–acaroid resin [7] showed an abrupt decrease in the ignition temperature by nearly 200 K with increasing heating rate which was superimposed on an underlying steady decrease.

Analysis of experimental results obtained under non-ignition conditions is reasonably secure. The effect of heating rate on the temperature of the sample corresponding to the maximum rate of reaction (T_{max}) has been represented by the relationship [1]

$$d(\ln \beta/T_{max}^2)/\ dT_{max}^{-1} = -E/R \qquad (1)$$

where β is the heating rate and E is the activation energy. Both the explosive and the pyrotechnic mixture containing boron and barium chromate gave results which could be represented by straight-line plots of $\ln \beta/T_{max}^2$ against T_{max}^{-1}. The results for the explosive are shown in Fig. 3. The value derived for the activation energy was 121 ± 3 kJ mol^{-1}. The pre-exponential factor $\ln[A\ (s^{-1})] = 21.7 \pm 0.7$ was obtained by assuming the reaction to be first order. To avoid ignition it was necessary to restrict the mass of the sample to < 1 mg and the heating rate to $\leqslant 50$ K min^{-1}. Furthermore, the experiments were carried out using the power-compensated DSC since its mode of operation further limits ignition.

The boron mixture gave results which showed a greater scatter and the activation energy $E = 330 \pm 30$ kJ mol^{-1} was less well defined. The validity of the analysis is open to question since the thermal analysis curve (Fig. 1) indicated the presence of two reactions with the possibility that the high temperature reaction, indicated by the shoulder, contributed to the peak maximum. The results for the tungsten mixture gave a distinctly curved plot of $\ln \beta/T_{\max}^2$ against $T_{\max}^{-1}$. This lack of success focuses attention on the different natures of the reaction regimes in the two pyrotechnics. The onset temperature of the reaction in the boron mixture is considerably below the melting temperature of the oxidant (> 1500 K). For the tungsten mixture chemical reaction is accompanied by melting of the potassium nitrate with a reaction rate in the liquid phase considerably greater than in the solid phase. The rate of melting dominates the shape of the initial portion of the thermal analysis curve. Even for the explosive there is uncertainty in the extent to which the reaction may occur in the gas phase. The DTA–TG curves indicated a mass loss accompanying an endothermic drift immediately preceding the exotherm.

The development of a realistic model for the ignition experiment is a formidable problem. Invariably solutions are only accessible by numerical processing. We have taken up a quite different stance by using a primitive model of the experiment based on Semenov boundary conditions [8] to seek analytical solutions which can be tested experimentally. The temperature evolution is described by the equation,

$$V\sigma C\, \mathrm{d}T/\mathrm{d}t = VQA \exp(-E/RT) - HS(T - T_a) \qquad (2)$$

It is assumed that the temperature of the sample is uniform and that the isothermal rate law is of zero order, i.e. reactant consumption is ignored. In eq. (2) V and S are the volume and surface area of the sample respectively. Q is the exothermicity per unit volume, and σ and C are the density and specific heat capacity respectively. The term $A \exp(-E/RT)$ represents the fractional extent of reaction, E and A are the activation energy and pre-exponential factor and H is the heat transfer coefficient. In the thermal analysis experiments the ambient temperature is increased linearly with time:

$$T_a = T_i + \beta t \qquad (3)$$

where T_i is the initial temperature. We further simplify the approach by assuming that prior to an instant of transition the system is chemically inert and afterwards the chemical reaction takes place under adiabatic conditions. Thus we obtain

$$V\sigma C\, \mathrm{d}T/\mathrm{d}t = -HS(T - T_a) \qquad (4)$$

and, after ignition,

$$\sigma C\, \mathrm{d}T/\mathrm{d}t = QA \exp(-E/RT) \qquad (5)$$

The transition temperature may be derived by equating the temperatures defined in eqns. (4) and (5) and their corresponding time derivatives. Further manipulation gives the ambient temperature T_{ign} at which the reactant temperature grows to infinity:

$$T_{\mathrm{ign}} = \beta t_{\mathrm{th}} + T_{\mathrm{Ar}}/\ln(A\, \Delta T_{\mathrm{ad}}/\beta) + T_{\mathrm{Ar}}/[\ln(A\, \Delta T_{\mathrm{ad}}/\beta)]^2 \qquad (6)$$

where $t_{th} = V\sigma C/HS$ is the thermal relaxation time of the inert system, $T_{Ar} = E/R$ is the Arrhenius temperature and ΔT_{ad} is the adiabatic temperature rise (Q/C). Equation (6) can be cast in the form

$$T_{ign} = p_1\beta + p_2/\ln(p_3/\beta) + p_2/[\ln(p_3/\beta)]^2 \tag{7}$$

in which p_1, p_2 and p_3 are constants: $p_1 = t_{th}$, $p_2 = T_{Ar}$ and $p_3 = A\ \Delta T_{ad}$.

Equation (7) provides an excellent description of the trend in the results which show initially a rapid rise in T_{ign} leading to an almost linear increase as the heating rate is increased. The expression for T_{ign} (eqn. (7)) has been derived assuming "ideal" instrument behaviour and the experimental values have incorporated the temperature calibration at the relevant heating rate. The differences between the results for the three materials are most pronounced at low heating rates: at high heating rates the variation is similar. The form of the relationship suggests that at high heating rates the predominant effect is one of thermal relaxation. The curves shown in Fig. 2 have been calculated from the experimental data using an iterative procedure (NAG library routine E04 CCF) to obtain the constants p_1, p_2 and p_3. The quality of the fit for the explosive is particularly good. A more rigorous test is to compare the values derived for the physicochemical parameters of the system with those obtained by more certain experimental routes. This pertains to the explosive and boron pyrotechnic mixture where the activation energies are available from the non-ignition experiments. The values derived from p_2 were 736 kJ mol^{-1} (explosive) and 1000 kJ mol^{-1} (boron pyrotechnic) which are at variance with the results obtained from the non-ignition experiments. The activation energy derived for tungsten–potassium nitrate was 323 kJ mol^{-1} which is what might reasonably be expected but probably fortuitously so. It would seem that eq. (7) is an acceptable representation of the experimental data judged entirely on an empirical basis but any attempt to use the model to obtain kinetic parameters is likely to lead to values which are erroneous. Values for the thermal relaxation time t_{th} obtained for the pyrotechnic mixtures, i.e. 7 s (boron pyrotechnic) and 4 s (tungsten pyrotechnic), were in reasonable accord with the response time expected for the apparatus and sample. However, the value obtained with the explosive (24 s) was significantly in error. The present results highlight the obvious inadequacies of the primitive model of the experiment. More complete descriptions are available [9] but the conceptual simplicity is lost and the solutions do not lead to a simple interpretation of the experimental results.

SUMMARY

Fundamental to the derivation of kinetic parameters from dynamic experiments is the assumption that the temperature of the sample is uniform

and varies linearly with time. With large samples and high heating rates temperature excesses may be established which can lead to thermal runaway and ignition of the sample. It was impossible to probe systematically the critical region where there was significant self-heating without thermal runaway. Not only was the region small but control over the experimental variables was insufficiently fine. An alternative approach in the derivation of kinetic parameters is to model the ignition experiment in an attempt to provide an interpretation of the experimental measurements. At first sight the variation of ignition temperature with heating rate offers a convenient empirical approach. The simple ignition model is attractive — it presents an easily comprehended description of the experiment and reproduces the general shape of the results. Unfortunately, it fails when the values of the parameters are examined in the light of their physicochemical significance. The influence of the kinetic parameters is most clearly observed at low heating rates: at higher heating rates it is the thermal relaxation which is the dominant factor. More complex models may produce a better description of the experiment but they do not provide a simple solution to the inverse problem of obtaining the kinetic parameters from the experiment.

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