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TIMES-TO-IGNITION OF PYROTECHNICS

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ABSTRACT

Times-to-ignition have been measured for pyrotechnic mixtures using a temperature-jump technique. The results obtained under highly supercritical conditions have been used to derive the chemical activation energies. Times-to-ignition under marginally supercritical conditions have been shown to obey the relationship $t_{\text{ign}} \propto 1/\sqrt{(\text{degree of supercriticality})}$.

INTRODUCTION

The measurement of times-to-ignition has proved to be a popular route to chemical activation energies in explosives, propellants and pyrotechnics. A wide range of experimental techniques has been used, from simple hot plate experiments to the use of specially designed equipment. The aim is to raise the temperature of the reactant as rapidly as possible from an initial value T_{i} to a value T_{a} above the critical temperature. The usual route to the activation energy is from the gradient of ln t_{ign} plotted against T_{a}^{-1}, i.e. assuming a relationship of the form

$$t_{\text{ign}} = \exp(E/RT_{\text{a}}) + C \tag{1}$$

where C is a temperature-independent constant.

The theoretical prediction of times-to-ignition for experimental configurations presents a formidable problem with a dearth of information on the relevant heat transfer coefficients. Generally, progress can only be made by making sweeping assumptions. Under adiabatic conditions the expression

$$t_{\text{ad}} = \frac{\sigma c R T_{\text{a}}^2 \exp(E/RT_{\text{a}})}{QEA} \tag{2}$$

may be derived [1], albeit ignoring reactant consumption. The process envisaged is one in which the reactant is initially dispersed at temperature T_{a} without self-heating and assembled at a time zero under adiabatic conditions. In practice, few experiments adhere to the principles embodied in this

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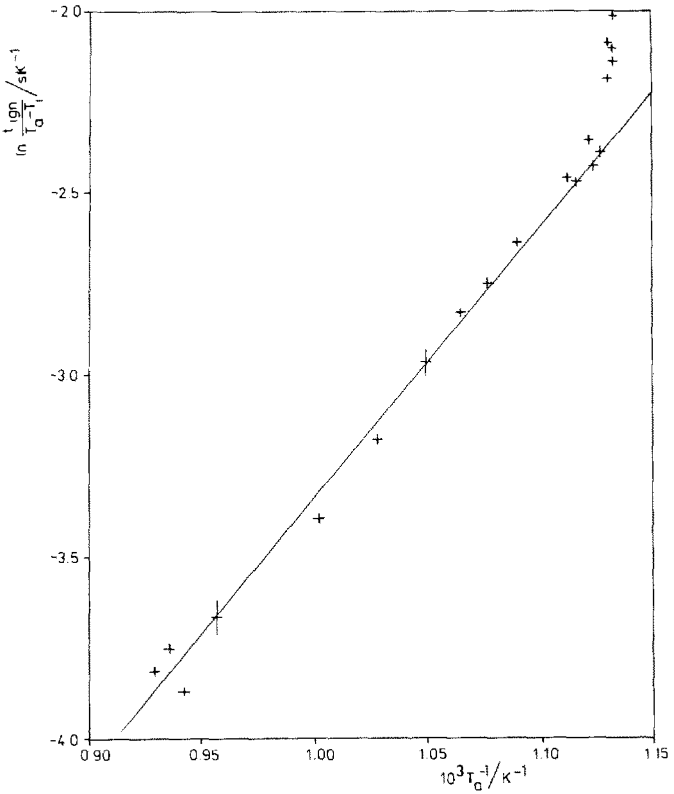

Fig. 1. Evaluation of the activation energy for a mixture of Mg and $KClO_4$ from measurements under highly supercritical conditions.

equation. Quite the reverse, most experiments require a considerable heat flux between the environment and the reactant. Nevertheless, it transpires that t_{ad} is a useful scale of time in expressing times-to-ignition. A further difficulty arises when the measurements are made under conditions only just supercritical when times-to-ignition become long. The interpretation is not straightforward, notwithstanding the possible increase in the precision of the time measurements.

The present investigation has been concerned with three pyrotechnic mixtures using thermal analysis equipment to heat the samples. Such equipment is commonly available: the particular model used (Stanton-Redcroft, DTA 674) has a large cylindrical furnace which can be pre-heated to the desired temperature and then rapidly lowered over the reactant. Thermal analysis has been used extensively to study pyrotechnic reactions including the ignition regime [2]. The results shown in Figs. 1–3 are for a mixture of Mg and $KClO_4$ and illustrate the trends observed in the other mixtures. The numerical results for all the pyrotechnics are given in Tables 1 and 2.

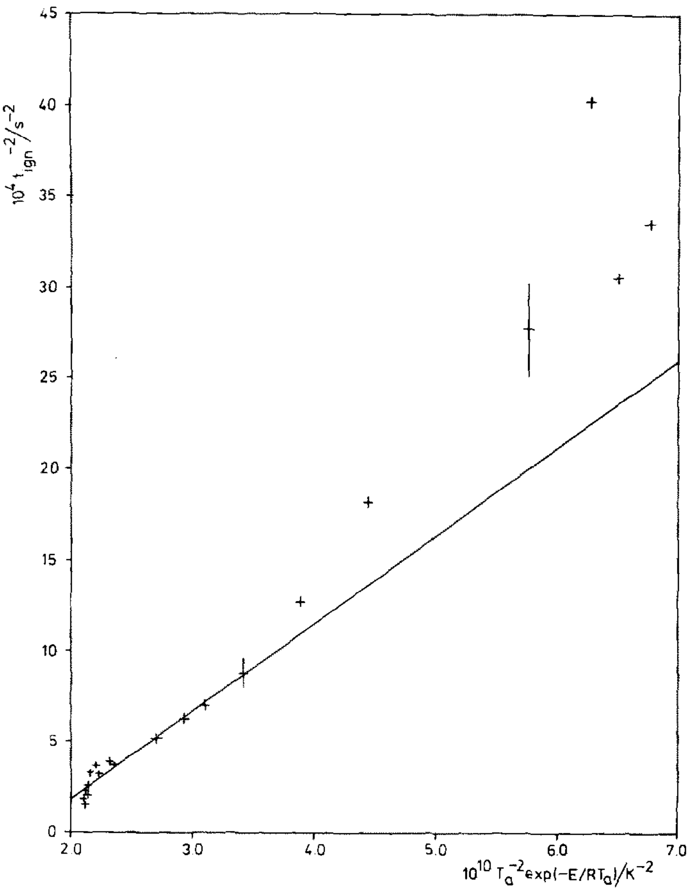

Fig. 2. Evaluation of T_{cr} for a mixture of Mg and $KClO_4$ from measurements near criticality. $E = 64 \pm 4$ kJ mol^{-1}.

EXPERIMENTAL

The three pyrotechnic mixtures studied and the masses used in experiments are as follows *: 11% B–89% MoO_3 (75 mg); 20% Mg–80% $KClO_4$ (100 mg); 15% lamp black–85% KNO_3 (30 mg). Preliminary experiments established that these masses were in excess of the critical values. The mixtures were lightly compacted into quartz or platinum crucibles to give cylindrical samples 4 mm in diameter and 4–6 mm in height. The DTA equipment incorporated a single stem head with a platinum–platinum/13% rhodium plate thermocouple. This head was sufficiently robust to withstand the ignition experiments without being damaged. The experiments were

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* In expressing the composition of mixtures, % = weight of component × 100/weight of mixture.

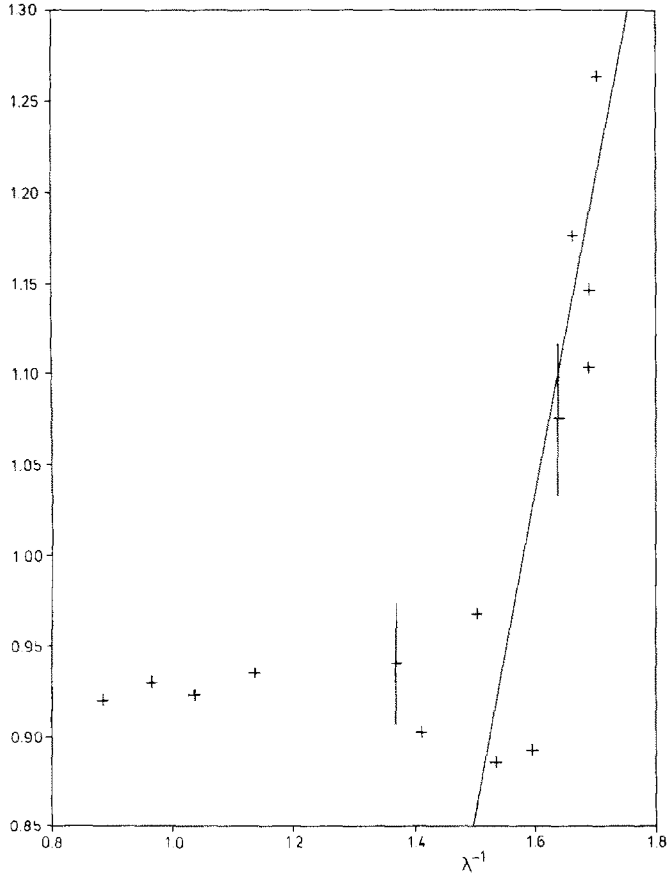

Fig. 3. Test of the relationship $\tau = M\lambda^{-1} + N$ for marginally supercritical conditons for a mixture of Mg and $KClO_4$. $E = 68$ kJ mol^{-1}, $T_{crit} = 848$ K.

TABLE 1

Activation energies derived from times-to-ignition measurements (kJ mol^{-1})

	B/MoO_3	$Mg/KClO_4$	C/KNO_3
Equation (1)	40 ± 3	53 ± 4	142 ± 3
Equation (2)	56 ± 3	68 ± 3	154 ± 3
Equation (4)	52 ± 3	64 ± 4	151 ± 3

TABLE 2

Test of relationship $\tau = M\lambda^{-1} + N$ for marginally supercritical conditions

	B/MoO_3	$Mg/KClO_4$	C/KNO_3
T_{cr} (K) [a]	758 ± 9	849 ± 9	698 ± 7
T_{cr} (K) [b]	760 ± 9	848 ± 10	699 ± 7
$t_{ad}(T_{cr})$ (s) [b]	48 ± 9	84 ± 12	933 ± 88
M [b]	1.3 ± 0.1	1.5 ± 0.4	0.9 ± 0.3
N [b]	-0.9 ± 0.1	-1.4 ± 0.6	-0.3 ± 0.5

[a] Activation energy derived from eqn. (4).

[b] Activation energy derived from eqn. (2).

carried out with a static atmosphere of argon in the apparatus to avoid aerial oxidation of the pyrotechnic fuels. The temperature of the furnace was stabilised whilst in its lower working position. The furnace was then raised, the crucible placed in the head and the furnace lowered again. The sample temperature was recorded on a chart recorder. Ignition was identified by a single sharp exotherm in which the measured temperature rise often exceeded 100 K. The ignition time was measured from the initial temperature rise when the furnace was lowered to the extrapolated onset of the leading edge of the ignition peak. In some experiments ignition was observed using a mirror to view the sample through the furnace.

RESULTS AND DISCUSSION

Thermal ignition theory has been reviewed by Merzhanov and Averson [1]. These authors expressed the results of numerical calculations for a reactant exposed to a constant high surface temperature by the equation

$$\ln\left(\frac{t_{\mathrm{ign}}}{T_{\mathrm{a}}-T_{\mathrm{i}}}\right)=\frac{E}{RT_{\mathrm{a}}}+\ln\left[0.2\frac{\sigma c}{QA}\left(\frac{E}{R}\,\frac{T_{\mathrm{a}}-T_{\mathrm{i}}}{T_{\mathrm{a}}^{2}}+b\right)\right] \tag{3}$$

where b has the value 8 for ignition. The model is that of a semi-infinite reactant in which consumption is ignored. Even so, the relationship suggests a route to examine experimental data. The second term on the right-hand side is only weakly temperature dependent and the equation may be represented as

$$\ln\left(\frac{t_{\mathrm{ign}}}{T_{\mathrm{a}}-T_{\mathrm{i}}}\right)=\frac{E}{RT_{\mathrm{a}}}+D \tag{4}$$

The results of the analysis are shown in Fig. 1: the data may be represented by a straight line when obtained from experiments under highly supercritical conditions but there is an increasing divergence as the conditions become only marginally supercritical. In principle, we may refine the approach by an iterative procedure in which allowance is made for the weak temperature-dependence of D. In practice, the experimental data are insufficiently precise for the analysis to be meaningful. Indeed, we observe that the data may equally well be represented by the relationships expressed in eqns. (1) and (2). The activation energies from the different approaches are shown in Table 1. Bearing in mind the experimental errors, there is no significant difference between the values for each of the pyrotechnic mixtures derived from eqns. (2) and (4). For comparison we have the value $E = 142$ kJ mol^{-1} for a mixture of Mg and $KClO_4$ obtained by time-to-ignition experiments in which the sample was immersed in a bath of molten lead [3]. For mixtures of carbon and KNO_3, values of the activation energy have been reported [4,5] but they vary widely (59–437 kJ mol^{-1}) depending on the source of the carbon. The range of ignition times for the mixtures of B–MoO_3 and Mg–$KClO_4$ was very restricted (12–73 s), whereas for the mixture of lamp black and KNO_3 the times extended to over 900 s.

We now turn our attention to the measurements under marginally supercritical conditions. Boddington et al. [6] have derived an expression for the time-to-ignition ignoring reactant consumption, in the approximate form

$$\tau_{\text{ign}} = \frac{t_{\text{ign}}}{t_{\text{ad}}} = M\lambda^{-1} + N \tag{5}$$

where $\lambda = (\delta/\delta_{\text{cr}} - 1)^{1/2}$ represents a small departure from criticality and $\delta = a_0^2 QEA \exp(-E/RT_{\text{a}})/\kappa RT_{\text{a}}^2$ is the Frank–Kamenetskii reduced reaction rate parameter. M and N are constants evaluated numerically. M is dependent on the reaction geometry and Biot number but in nearly all cases is about 1.5; N is -0.8 for spherical geometry when the reactant edge temperature is held constant. Under conditions close to criticality we have $t_{\text{ign}} \propto 1/(\delta/\delta_{\text{cr}} - 1)^{1/2}$ and we may plot t_{ign}^{-2} against $T_{\text{a}}^{-2} \exp(-E/RT_{\text{a}})$ in the expectation of obtaining a straight line. The results are shown in Fig. 2 where it is clear that the data may indeed be represented by a straight line in the vicinity of criticality. Extrapolation to $t_{\text{ign}}^{-2} = 0$ gives the value of $T_{\text{cr}}^{-2} \exp(-E/RT_{\text{cr}})$ from which T_{cr} may be obtained. Table 2 shows the results obtained using activation energies derived from both eqns. (2) and (4). The abscissa in Fig. 2 has been calculated using the activation energy from eqn. (4). The need to extrapolate the data to obtain T_{cr} demonstrates that there is a region close to criticality which is difficult to investigate experimentally. It is just this region where we might have expected eqn. (5) to become invalid due to reactant consumption. However, it has been shown [7] that the formula holds good except in a small region very near to criticality ($\leqslant 1$ K).

We may now examine the validity of eqn. (5) further by plotting τ_{ign}, i.e. $t_{\text{ign}}/t_{\text{ad}}$ against λ^{-1}. This requires a knowledge of the term $\sigma c/QA$ to calculate t_{ad}. Once again there are alternative approaches but here very different results are obtained. If we derive $\sigma c/QA$ from the intercept of $\ln t_{\text{ign}}/T_{\text{a}}^2$ plotted against T_{a}^{-1} (eqn. 2), we obtain the graph shown in Fig. 3. It is possible to represent the data close to criticality by a straight line although the errors in the data points are large. However, it is remarkable that the gradients for the three pyrotechnic mixtures (Table 2) not only agree within the experimental errors but are close to the theoretical value, $M \approx 1.5$. The values of t_{ad} at the critical temperature are also shown in the Table. The other approach is to obtain $\sigma c/QA$ from the intercept:

$$D = \ln\left[0.2 \frac{\sigma c}{QA} \left(\frac{E}{R} \frac{T_{\text{a}} - T_{\text{i}}}{T_{\text{a}}^2} + 8 \right)\right]$$

As before, a linear relationship is observed between τ and λ^{-1} but the gradients are no longer in agreement and are significantly greater than the theoretical value. The result is contrary to expectations since we would have expected this approach to be superior to that based on eqn. (2).

SUMMARY

The times-to-ignition under highly supercritical conditions have been interpreted using the three approaches expressed by eqns. (1), (2) and (4). The measurements are not sufficiently precise to discriminate between these approaches, and the derived activation energies agree reasonably closely. No attempt has been made to correct for an "assembly time" in which the sample attains the temperature T_a. The results do indicate the need to make measurements over as wide a temperature range as possible in order to identify the region of high supercriticality. The danger is that activation energies will be derived from measurements under conditions which are not supercritical enough so that erroneous values of E will be obtained.

The expression for times-to-ignition under marginally supercritical conditions does not lend itself to the ready evaluation of activation energies. This is unfortunate in view of the greater precision often observed in the measured times. In the region very near to criticality the times become extremely sensitive to the experimental conditions. Here it may not be possible to reproduce the experiment sufficiently closely to obtain consistent results. We have used the values of E and $\sigma c/QA$ derived from measurements under highly supercritical conditions in an attempt to confirm the expression. In partial confirmation, we have observed a linear relationship, between τ and λ^{-1} ($\delta/\delta_{cr} \lesssim 1.5$) but large errors are incurred in the calculation of t_{ad} and λ. We are unable to derive the values of the constants M and N with certainty because they depend on the model used to interpret the experiments under highly supercritical conditions. If the "adiabatic model" is used (eqn. 2), the values of M are remarkably close to that derived theoretically. The underlying theory invokes heat transport wholly by conduction so that the agreement shown by the results for the mixture of lamp black and KNO_3 is more surprising still, in view of the gassy nature of its combustion reaction.

We have investigated the two extremes of ignition behaviour. On the one hand we have the highly supercritical region, and on the other the marginally supercriticial when times-to-ignition become long. We have discerned some agreement between the experimental results and theory. Where there is lack of agreement the cause may lie in an inadequate description of the temperature change experienced by the reactant. The indications are that the intermediate region of moderate supercriticality is rather small.

ACKNOWLEDGEMENTS

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NOTATION

A	pre-exponential factor
a_0	scale distance for reactant mass
c	specific heat capacity of the reactant mixture
C	constant in eqn. (1)
D	constant in eqn. (4)
E	activation energy
M	constant in eqn. (5)
N	constant in eqn. (5)
Q	molar exothermicity of reactant mass
R	universal gas constant
t	time
T	thermodynamic (absolute) temperature

Greek letters

κ	thermal conductivity of reactant mass
δ	Frank-Kamenetskii's reduced reaction rate, $a_0^2QEA\exp(-E/RT_a)/\kappa RT_a^2$
λ	$[(\delta/\delta_{cr})-1]^{1/2}$, the small parameter of slightly supercritical systems
σ	density of reactant mass
τ	t_{ign}/t_{ad}

Subscripts

a	ambient value
ad	adiabatic value
cr	critical value
i	initial value
ign	value at ignition

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