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THERMAL EXPLOSION OF BENZOYL PEROXIDE

by

P. C. BOWES

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SUMMARY

The thermal explosion of benzoyl peroxide, in the form of the commercially pure solid and as a paste with plasticiser, has been studied experimentally with the object of determining the extent to which small-scale explosion trials are likely to provide a useful guide to the behaviour of unstable compounds in storage or during transport.

A comparison of (1) self-heating and explosion data and (2) isothermal decomposition data, principally in terms of the derived activation energies and of heats of reaction estimated by different routes, has shown that the self-heating and explosion behaviour is broadly consistent with expectation on the basis of the generalised stationary state thermal explosion model of Frank-Kamenetskii. In detail, the behaviour is complicated by melting of the peroxide during decomposition ^{and} by mixing due to gas evolution.

It has been concluded that a simple graphical treatment of small-scale critical explosion data, based on the model, can give a useful guide to the practical hazard.

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LIST OF SYMBOLS

a	"Constant" in equation (3)
A	Pre-exponential factor of Arrhenius equation
c	Specific heat
D	Diameter of cylinder
E	Activation energy
f	Proportionality factor (equation (12) and Table 3).
ΔH°	Standard heat of reaction Kg cal/mole
h	Average heat transfer coefficient at surface of cylinder
k	Rate constant
λ	thermal conductivity
K	"Constant" in equation (3)
L	Length of cylinder
N_{Nu}, N_{Pr}, N_{Re}	Nusselt, Prandtl and Reynolds numbers respectively.
Q	Heat of reaction cal/g
r	Radius of cylinder
T	Temperature ($^\circ\text{C}$ or $^\circ\text{K}$ as required). Subscripts A, s and o refer to ambient, surface and centre respectively.
t	Time
t_i	Induction period
x	Fraction reacted
α	hr/λ
β	Effective heat transfer coefficient (dimensionless)
δ, δ_c	Frank-Kamenetskii self heating parameter, equation (6)
θ_o	Dimensionless central temperature rise, equation (6)
ρ	Density

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INTRODUCTION

Theoretical models of thermal explosion, developed initially for explosion in gaseous systems^{1, 2}, provide a useful approach to practical problems of self-heating and ignition in solids and liquids which are subject to appreciable decomposition or reaction at relatively low temperatures. This paper reports a study of the thermal explosion of benzoyl peroxide, at temperatures below its melting point, which has been carried out as part of a research programme concerned with the assessment of self-heating and explosion hazards associated with the storage and transport of unstable compounds.

Of the several experimental checks of the applicability of the theory that have been reported, those by Merzhanov and others^{3, 4, 5}, are most relevant to the purposes of the present study. These authors have shown that explosion characteristics calculated on the basis of the theory, from independently determined thermal and kinetic data, can agree closely with observed values for some molten explosives when the experimental conditions are adjusted to satisfy the Semenov model¹, i.e. with vigorous artificial stirring to annul temperature gradients in the melt. In an unstirred system⁵, the actual critical ambient temperatures for explosion lay between the values calculated for the Semenov and Frank-Kamenetskii² models and the sub-critical temperature increases were much higher than expected. These discrepancies were attributed to a progressive change in the effective heat transfer coefficient for the system which was associated with gas evolution in the molten explosive.

In the present work the approach has been to determine experimentally the critical ambient temperatures for the explosion of charges of given shape and different sizes, and to express the results in terms of a linear relationship (based on the stationary-state thermal explosion model with a general boundary condition⁶) previously applied to the self-ignition of cellulosic materials⁷. This approach is simple and makes minimum demands on the theoretical model when used for extrapolation to practical conditions.

At the same time, a comparison has been made with the behaviour to be expected from the kinetics of the isothermal decomposition of the benzoyl peroxide used.

The peroxide has been examined in the form of the dry solid and as a paste with plasticiser. These are the forms in which the peroxide is used in practice, although use of the dry peroxide is becoming less common than hitherto. The isothermal decomposition follows a different course for the two systems, having an autocatalytic character for the dry peroxide and a relatively high initial rate, apparently of zero order, for the paste. Melting of the peroxide and mixing by gas evolution occurs during the self-heating to explosion, and some insight into the role of these phenomena in the thermal explosion process has been gained.

ISOTHERMAL DECOMPOSITION

Rate equations

The materials used were solid benzoyl peroxide of commercial purity (about 98 per cent) and a paste of benzoyl peroxide with dimethyl phthalate containing 65 per cent peroxide. The isothermal decomposition of these materials at temperatures in the range 50 - 90°C has been described elsewhere^{8, 9}, and only the main features and results applicable to the occurrence of thermal explosion under practical conditions will be summarised here.

The decomposition of the peroxide paste followed a simple course; the initial rate was the maximum and, at the lower temperatures, remained constant for up to 40 - 60 per cent decomposition. The maximum rate of decomposition of peroxide per unit weight of paste was thus given by

$$0.65 \frac{dx}{dt} = 0.65 k \quad (1)$$

where x is the fraction of peroxide decomposed in time, t . The zero order rate constant, k , was found to be

$$k = 10^{26.19} e^{\frac{-49300}{RT}} \text{ s}^{-1} \quad (2)$$

The decomposition was accompanied by liquefaction.

The fractional decomposition of the solid ("dry") peroxide showed the sigmoid variation with time common to many solids. A liquid phase appeared during the decomposition and the major part of the increase in the rate of decomposition occurred while liquid phase accumulated at the expense of solid phase, the rate of decomposition of peroxide dissolved in the liquid phase being greater than in the solid.

The course of the decomposition in this acceleratory stage was accounted for semi-quantitatively by an extension⁸ of a rate equation for decomposing solids proposed by Bawn¹⁰ and Manelis and Dubovitskii¹¹, which assumes quasi-equilibrium between the solid and liquid phases. This equation reduces to the form

$$\frac{dx}{dt} = K(x + \underline{a}) \quad (3)$$

where K and \underline{a} are both functions of the rate constants for the solid and liquid phase reactions and of the composition of the phases. The rate is a maximum when $x = x_1$, where x_1 is the degree of decomposition at which solid phase disappears. Although, in principle, K and \underline{a} are calculable from the relevant constants at a given temperature⁸, it was found that the accuracy was low and it was preferable to obtain K from the slope of a plot of experimental observations as $\log(x + \underline{a})$ against time (the calculated values for K were 20 - 40 per cent lower than these latter "observed" values). \underline{a} was small and calculated values were adequate.

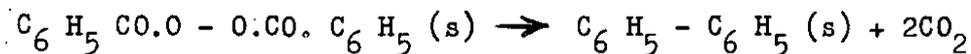
For purposes of determining critical conditions for thermal explosion of the "dry" peroxide, the maximum rates of decomposition given by equation (3) at different temperatures, with $x = x_1$ and "observed" values for K , can, over a limited range of temperature, be treated as rate constants for a hypothetical zero order reaction². An Arrhenius plot of these maximum rates gave a straight line in the temperature range 70 - 90°C (see Fig. 3 later) with the following equation for the "zero order" rate constant

$$k = 10^{26.11} e^{\frac{-50500}{RT}} \text{ s}^{-1} \quad (4)$$

Since the loss in weight of the dry peroxide was only about 18 per cent for complete decomposition, no correction for this was made to the rate equation¹¹.

Estimated heat of reaction

The mechanism of the decomposition was not investigated, but it was confirmed by comparative vapour phase chromatography that the principal condensed products of the solid benzoyl peroxide within the temperature range covered by the thermal ignition experiments (74°C - 90°C) were diphenyl, phenyl benzoate and benzoic acid and, also, that these products appeared in comparable quantities. It may, therefore, be expected that the heat of reaction for decomposition of the dry peroxide will lie between the values for the following overall reactions:-



$$\Delta H^\circ = -72.2 \text{ kcal/mole}$$



$$\Delta H^\circ = -54.8 \text{ kcal/mole}$$

In these equations the heats of reaction have been estimated from a recent value for the heat of combustion of benzoyl peroxide¹² and earlier tabulated values¹³ for diphenyl and phenyl benzoate.

Mörssi¹⁴ found that, at higher temperatures, 95 - 115°C, the principal condensed product of the decomposition of benzoyl peroxide (at least in vacuo) was phenyl benzoate with only a trace of diphenyl and no benzoic acid. This observation, when compared with the admittedly qualitative observations of the present work, suggests that the heat of reaction may decrease with increasing temperature, i.e. from about 72 kcal/mole at low temperatures to about 55 kcal/mole at higher temperatures (or from about 300 to 230 cal/g).

THEORETICAL MODEL FOR THERMAL EXPLOSION

The relatively high heat of reaction justifies the neglect of reactant consumption and the use of the stationary state theory for predicting critical conditions for thermal explosion².

In the explosion experiments (see below) it was convenient to use cylindrical containers for the peroxide, and the experimental conditions were such that the surface heat transfer coefficient for the containers, h , and the corresponding heat transfer parameter, λ/r , for the contents were comparable magnitudes. The parameters of the stationary state thermal explosion model appropriate to this system have been derived elsewhere¹⁵, and the results required in the present paper may be outlined as follows:

Using the exponential² and "effective transfer"^{2, 16} approximations, the equation for the heat balance in the stationary state for an exothermic reaction obeying the Arrhenius equation in a cylinder of length L and radius r becomes, in dimensionless form,

$$\delta e^{\theta_0} = 2 \frac{L+r}{L} \beta \theta_0 \quad (5)$$

where δ is the Frank-Kamenetskii self-heating parameter, and θ_0 the dimensionless temperature rise at the centre, each defined in the usual way as

$$\delta = \frac{E}{RT_A^2} \frac{\rho r^2}{\lambda} Q_A e^{-E/RT_A} \quad (6i)$$

$$\theta_0 = \frac{E}{RT_A^2} (T_0 - T_A) \quad (6ii)$$

and β is the effective heat-transfer coefficient. δ has its maximum, or critical, value, δ_c , when $\theta_0 = 1$ in equation (5).

β is a function of α , where $\alpha = hr/\lambda$ and h is, here, an average heat transfer coefficient, for heat transfer by convection and radiation, for all surfaces of the cylinder. Evaluation of β by the approximate procedure of Frank-Kamenetskii² and Thomas¹⁶, yields $\delta_c(\alpha, L/D)$ as

$$\delta_c = \frac{1}{e} \left[\mu^2 + \left(\gamma \frac{D}{L} \right)^2 \right] \quad (7)$$

where γ is the first root of

$$\gamma \tan \gamma = \alpha D/L$$

and μ is the first positive root of

$$\mu J_1(\mu) = \alpha J_0(\mu)$$

where J_1 and J_0 are Bessel functions.

When $\alpha = \infty$, equation (7) reduces to the equation obtained by Frank-Kamenetskii², who found that this approximate procedure tended to give values of δ_c about 8 per cent higher than those which could be obtained analytically for certain geometries without approximation of the conduction terms in the full equation for the heat balance. In this paper, values of δ_c calculated from equation (7) have accordingly been reduced by 8 per cent.

The critical temperature rise for thermal explosion in the short cylinder may be estimated by a comparative method due to Wake and Walker¹⁷. Extending their approach to the comparison of critical temperature increases at a given ambient temperature, and using the approximate proportionality of the α correction for different geometries as recently justified by Merzhanov¹⁸, we have, in the notation of the present paper,

$$\theta_0(\alpha, L/D)_{\text{cylinder}} \doteq \frac{6}{4} \theta_0(\alpha)_{\text{sphere}} \times N_1 \left(\frac{L}{D} \right) \frac{\delta_c(\infty, L/D)_{\text{cylinder}}}{\delta_c(\infty)_{\text{sphere}}} \quad (8)$$

where $N_1(L/D)$ is a function calculated by Wake and Walker for the finite cylinder with heat generation at a rate independent of temperature, and $\theta_0(\alpha)_{\text{sphere}}$ is

the critical temperature rise at the centre of a sphere, at given α , for a reaction obeying the Arrhenius equation⁶. For an infinite cylinder with $\alpha = \infty$, the estimate of the critical value of θ_0 given by equation (8) is five per cent higher than the value given by solution of the self-heating equation with a reaction rate obeying the Arrhenius equation.

The temperature rise due to self-heating in a cylinder in a sub-critical state may be estimated from the following equation (for small values of the temperature rise):-

$$T_0 - T_A = \frac{\alpha + 2}{\alpha} N_1 \left(\frac{L}{D}\right) \frac{r^2 \rho}{4\lambda} Qk(T_0) \quad (9)$$

This equation is based on the assumption that the sub-critical temperature rise is equal to the central value $(T_0 - T_A)$ everywhere in the cylinder⁷; it also includes the correction due to Wake and Walker¹⁷, for $L/D < \infty$.

The corresponding equation for a sphere⁷ (for which $N_1(L/D)/4 = 1/6$) underestimates $(T_0 - T_A)$ by about 12 per cent when $\theta_0 \doteq 0.4$, in comparison with a more exact equation based on Chambre's analysis⁷ ($(T_0 - T_A) \doteq 2^\circ\text{C}$ when $\theta_0 = 0.4$ and $E \doteq 47,000$). It will be assumed below that a similar error will arise for the finite cylinder.

For the purpose of estimating α from observations of temperature during self-heating, it may be noted that, in terms of the "effective transfer" approximation, the heat balance between the cylinder and its surroundings in a steady state is given by

$$\alpha (T_s - T_A) = \beta_{\infty} (T_0 - T_s) = \beta (T_0 - T_A) ;$$

whence

$$\alpha = \beta_{\infty} \frac{T_0 - T_s}{T_s - T_A} \quad (10)$$

where β_{∞} is the value of β at $\alpha = \infty$ and is calculated from equation (5) by inserting the value of S_c for $\alpha = \infty$. For the cylinder having $L/D = 1.6$, as used in the present work, this value of S_c is 2.33 and β_{∞} is 2.42. Here, strictly, T_s is the average temperature for all surfaces of the cylinder; in practice (as below) it may be estimated from measurements at a point on the surface.

EXPERIMENTAL

The experimental methods and equipment, together with the safety precautions, are described in detail elsewhere¹⁹ and will here be only briefly indicated.

Explosion experiments

Minimum temperatures for the thermal explosion of dry benzoyl peroxide, in open-topped containers of different sizes, were determined by successive trials in a vertical cylindrical furnace provided with explosion relief vents. The furnace was heated electrically and its nominal temperature was controlled to within $\pm 0.3^{\circ}\text{C}$. The temperature in the working space of the furnace (19.0 cm diameter by 28.5 cm high) was maintained uniform to within $\pm 0.5^{\circ}\text{C}$ of the value at the centre by means of a circulating fan. The progress of self-heating in a sample of peroxide, relative to the furnace, was observed by means of a differential thermocouple at the centre. A second thermocouple was tied to the side of the sample container to give an indication of the surface temperatures, but it was difficult to make a satisfactory thermal contact here and the temperatures indicated were probably low. The explosion of quantities of up to 30 g of dry peroxide was studied in this way. The cylindrical sample containers were of aluminium and had a height to diameter ratio of 2; they were filled with peroxide to a height of 1.6 times the diameter.

Explosion studies with the peroxide paste were made with larger quantities, up to 800 g, and for this purpose the experimental method of Merzhanov and others³⁻⁵ was used. Open-topped cylindrical containers for the peroxide were supported in expendable heating jackets made of sheet steel through which water was circulated from a constant temperature system. The sample container was separated from the inner surface of the jacket by spacers to give a narrow air gap and the open end of the jacket was closed with light-weight thermal insulation. The temperature of the heating water was controlled to within about $\pm 0.05^{\circ}\text{C}$. Again, self-heating was observed by means of a differential thermocouple at the centre, and a second couple, inserted at about the centre of the inside surface of the sample container, indicated the surface temperature for purposes of estimating α .

Heat transfer measurements

Surface heat transfer coefficients, h , for the sample containers in the stirred working space of the furnace used for the "dry" peroxide were estimated with the aid of the following equation, for spherical bodies, due to Ranz and Marshall²⁰

$$N_{Nu} = 2 + 0.6 N_{Pr}^{\frac{1}{3}} N_{Re}^{\frac{1}{2}} \quad (11)$$

The characteristic air velocity for the system, required in the Reynolds Number in this equation, was obtained from experimental measurements of the heat transfer coefficient for two sizes of solid aluminium cylinder, electrically heated, in the furnace¹⁹. These experimental values, inserted into equation (11) together with appropriate constants for air at 80°C, yielded a mean value of 353 ± 15 cm/sec for this velocity. The required heat transfer coefficients based on this approach, are given in Table 1 below.

Assuming an emissivity as high as 0.2 for the clean aluminium surfaces, the heat transfer by radiation at a temperature 5°C in excess of the furnace was estimated as only about 5 per cent of the convective transfer and was therefore ignored.

The air gap between the sample containers and heating jackets, used for the explosion experiments with the paste, was of the order of 3 mm so that heat transfer was conductive rather than convective²¹ (Rayleigh number of order 10^5 for 4 cm container). For the 4 cm container, the air gap was 3.5 mm and measurement¹⁹ of the average heat transfer coefficient (including losses via the neck insulation) yielded a value of 4.2×10^{-4} cal cm⁻²s⁻¹ degC⁻¹. This is in reasonable agreement with the calculated value of 3.3×10^{-4} for heat transfer across the air gap alone by conduction and radiation, assuming an emissivity of about 0.6 for an oil-contaminated aluminium surface²²; the excess is doubtless largely due to neck losses.

RESULTS

General

Figures 1 and 2 show temperature/time records for the self-heating and explosion of the "dry" peroxide and the peroxide paste. These examples have been chosen as showing, most clearly, details of behaviour relevant to the interpretation of certain of the quantitative results below. The resolution of these details depended rather sharply on the nearness of the ambient temperature to the critical value for a given size of charge.

It will be seen that, for the two examples of explosion, the central temperature actually decreased for a period shortly before the explosion occurred and that, during this period, the temperature at the surface increased sharply to the central value.

Table 1

Thermal explosion of dry benzoyl peroxide
in cylindrical containers

Charge diameter cm	Critical temperature °C	ΔT_{\max} °C	h cal cm ⁻² s ⁻¹	α		S_c	
				granular solid	molten	(L/D = 1.6)* granular solid	(L/D = 0.7)* molten
0.86	90.8	8.0	18×10^{-4}	5.7	2.3	1.6	2.0
1.39	85.0	9.5	14×10^{-4}	7.1	2.8	1.7	2.2
1.91	81.4	8.0	12×10^{-4}	8.1	3.3	1.8	2.4
2.67	78.2	7.5	10×10^{-4}	9.6	3.8	1.9	2.5
3.72	74.0	2.5	8.4×10^{-4}	11	4.5	1.9	2.7

* $N_1(1.6) = 0.95$, $N_1(0.7) = 0.6$

On several occasions, as in the example of Fig. 1, the central temperature showed two maxima in sub-critical trials with the "dry" peroxide. This effect tended to occur most often with the smaller charges and higher temperatures; it was not observed at all in sub-critical trials with the paste.

These effects, and others which will be noted in the detailed analysis of the results, may be ascribed to melting of the charge and mixing by gas evolution. Their consequences for the application of the thermal explosion model are considered further in the Discussion.

Explosion was sharply defined with respect to changes in ambient temperature. Thus the distribution of explosion frequencies was as follows below for "dry" peroxide in containers 1.39 cm in diameter:-

Ambient temperature, °C	84.8 - 85.0	85.1 - 85.2
Explosion frequency	1/5	3/5

Although not investigated further in a systematic manner, the above distribution, in conjunction with experience with other sizes of container, suggested that the critical temperatures determined were likely to have been within $\pm 0.5^\circ\text{C}$, or better, of the value for 50 per cent explosions.

Nature of explosion

At temperatures near the critical, the "dry" peroxide usually exploded with a report and blew aluminium foil pressure relief vents out of the furnace. On one occasion, however, a charge in a container 4.0 cm diameter exposed for 22 hours to a temperature 7°C above the critical value, exploded with sufficient violence to fragment the open-topped aluminium container²³.

Thermal explosion of the peroxide paste was characterised by violent decomposition and expulsion of the contents of the container within a period judged to be of the order of a second. No damage was done to the container.

Critical data

Critical data obtained for the thermal explosion of the "dry" peroxide is given in Table 1, which also includes heat transfer coefficients estimated from equation (11) and the maximum temperature increase due to self-heating, in charges which did not explode (denoted ΔT_{max})

Values of α and S_c in Table 1 have been calculated for the solid in its initial granular state and also for the completely molten but gas-free mixture of products and undecomposed peroxide (using constants listed in the Appendix). In calculating α , it was necessary to assume that the heat-transfer coefficient, h , was independent of the length to diameter ratio of the charge in the container.

Apart from the effects of possible mixing, and additional heat loss due to gas evolution, the values of S_c relevant to thermal explosion of the decomposing peroxide may be expected to lie between those of the last two columns. The most probable condition of the peroxide near the critical state was that of a carbon dioxide foam of the molten material; at a density as low as that of the granular solid, such a foam would have a thermal conductivity substantially the same as that of granular solid (Appendix) - so the above limits for S_c are unaffected by this picture.

The critical data obtained for explosion of the benzoyl peroxide paste is given in Table 2.

Values of α in Table 2 were calculated from equation (10) using values of centre and edge temperatures taken from temperature/time records in the neighbourhood of an inflexion or a maximum, i.e. when a nearly steady state existed. The mean values of α are tabulated and their ranges indicated. Factors contributing to the variability in α are likely to have been errors in the positioning of the thermocouples and the centering of the container in the heating-jacket.

The mean values of α and the heat transfer coefficients were, in these experiments, used to estimate the thermal conductivity of the paste (Table 2). The values obtained are lower than expected for the paste in the absence of reaction (Appendix), and they decrease as the charge diameter decreases and the critical temperature increases. Since they are based on the temperature distribution in the paste before appreciable mixing occurred, these low values, and their dependence on temperature, are presumably associated with the accumulation of relatively immobile gas bubbles in the paste.

Table 2

Thermal explosion of benzoyl peroxide paste
in cylindrical containers

Charge diameter cm	Critical temperature °C	ΔT_{\max} °C	α	n*	S_c (L/D = 1.6)	h cal cm ⁻² s ⁻¹	λ cal cm ⁻¹ s ⁻¹ degC ⁻¹
2.7	71.8	12.5	3.4 ± 1.0	4	1.3 ± 0.2	6 x 10 ⁻⁴	2.4 x 10 ⁻⁴
4.1	66.5	9.7	3.2	1	1.0	4.2 x 10 ⁻⁴	2.7 x 10 ⁻⁴
5.0	64.7	7.5	3.5 ± 1.5	4	1.3 ± 0.3	4.2 x 10 ⁻⁴	3.0 x 10 ⁻⁴
8.0	59.9	12.0	4.3 ± 1.4	5	1.4 ± 0.2	4.2 x 10 ⁻⁴	3.9 x 10 ⁻⁴

*n = number of experiments for which values of α were available.

For the purpose of approximate comparison, it may be noted that the critical temperature for explosion of the paste was about 6°C lower than for the "dry" peroxide in containers of comparable diameter (2.67 and 2.7 cm). At a given temperature, the critical diameter for explosion of the paste is about half that for the "dry" peroxide.

Comparison of critical explosion results and kinetic results

It follows from the definition of δ_c , equation (6), that explosion results conforming to the stationary-state thermal explosion model should⁽⁷⁾, when plotted as $\log (\delta_c T_A^2/r^2)$ versus T_A^{-1} , fit a straight line of slope proportional to the activation energy. Explosion results for the "dry" peroxide and the paste given in Tables 1 and 2 are plotted in this way in Fig. 3. Points for the former are based on values of δ_c for the molten gas-free state ($L/D = 0.7$).

The "zero order" rate constants for the isothermal decomposition of the "dry" peroxide and the paste^{8, 9}, are also plotted in Fig. 3, against the reciprocals of the absolute temperature. In order to effect coincidence at about the middle of the ranges of the explosion data, the rate constants for the "dry" peroxide have been multiplied by 2.1×10^{10} , and those for the paste by 7.6×10^9 .

Over the range which it was practicable to study experimentally, the explosion results do, in fact, obey linear relationships in Fig. 3. Values of the apparent activation energies calculated from the slopes of the lines for the explosion results, namely 40,800 cal/mole for the "dry" peroxide and 44,800 cal/mole for the paste, are lower than the values obtained from the kinetic results (equations (2) and (3)).

At the points of coincidence of the explosion and kinetic results in Fig. 3, we have

$$k(T_A) f = \delta_c T_A^2 / r^2 = \frac{E + Qk(T_A)}{R\lambda} \quad , \quad (12)$$

where f is the factor used above to multiply the rate constants and $k(T_A)$ is the value of a rate constant at temperature T_A . The above equation may be used to estimate the heat of reaction, Q . Such estimates, based on physical data given in the Appendix and on mean values of the activation energies for the explosion results and kinetic results, are given in Table 3.

Table 3

Estimates of heats of reaction from comparison of explosion results and kinetic results

Material	State	Activation energy (mean) cal/mole	r/ρ	$f = \frac{S_c T_A^2}{r^2 k(T_A)}$	Heat of reaction cal/g
"Dry" benzoyl peroxide	molten	46,000	2.9×10^{-4}	2.10×10^{10}	270
	"foam"	46,000	3.0×10^{-4}	1.6×10^{10}	210
Benzoyl peroxide paste (35 per cent dimethyl phthalate)		47,000	$4.5 \times 10^{-4*}$	7.6×10^9	145 (paste) 223 (peroxide)
*Value for unreacted paste (Appendix)					

Since the density of the self-heating paste was not known, the ratio λ/ρ was assumed to be equal to the value estimated for the unreacted paste (Appendix). This value and, hence, the estimated value of the heat of reaction, may, however, be somewhat too high since it implies a volume increase by a factor of about two for the 2.7 cm diameter charge of peroxide paste in the immediately sub-critical state (Table 2). Although the increase in volume of the paste in sub-critical tests was always large enough to cause the paste to overflow from the container, it did not appear ever to have been as large as this.

The heat of reaction may also be estimated by application of equation (9) to observations of self-heating in sub-critical experiments, provided the temperature rise is small. Estimates obtained in this way, increased by 12 per cent (see remarks on equation (9) above) are given in Table 4. The values of α in Tables 1 and 2 for the "dry" peroxide in the molten state and for the paste were used in these calculations and the ratio λ/ρ for the paste was assumed to be constant and equal to the value used above in Table 3.

Table 4
Estimates of heat of reaction from self-heating

Material	Charge diameter cm	T_A °C	$T_o - T_A$ °C	Q cal/g
"Dry" peroxide (molten state)	3.7	74	2.5	224
	1.39	84	2.5	205
Peroxide paste	8.0	57	2.0	290*
	5.0	62	3.0	304*
	2.7	68	2.0	246*
* $\lambda/\rho = 4.5 \times 10^{-4}$				

The estimates of the heat of reaction, obtained by the two different methods, in Tables 3 and 4, lie within the range 255 ± 50 cal/g. This range includes the 210-270 cal/g expected on thermochemical grounds. In terms of the inverse calculation, an uncertainty of ± 50 cal/g in the heat of reaction (i.e. ± 20 per cent) implies an uncertainty of ± 10 per cent on an estimate of critical size, and of $\pm 1^\circ\text{C}$ on an estimate of critical temperature.

Critical temperature increase

Depending on the values of α and L/D , the dimensionless critical temperature increase, θ_0 , calculated for the "dry" peroxide by means of equation (8) is 1.4 - 1.6. This corresponds to an actual temperature increase of 8 - 9 degC. For the paste, the corresponding value of θ_0 is 1.5, which corresponds to a temperature increase of 7 - 7.5 degC.

Reference to Tables 1 and 2 shows that the maximum observed values for the sub-critical temperature increase barely exceeded the expected value for the "dry" peroxide but, for the paste, the expected value was exceeded by 5 degC.

Induction periods

The induction periods, t_i , for explosion and for isothermal decomposition of the "dry" benzoyl peroxide are plotted logarithmically against the reciprocal of the absolute temperature in Fig. 3. The induction periods for explosion were generally large and were measured simply as the time to actual explosion (Fig. 1); the induction periods for isothermal decomposition were measured as the time to the maximum rate of decomposition. Both sets of results lie closely about a common straight line; thus, at any given temperature, the occurrence of explosion is closely associated with the maximum rate of decomposition of the peroxide - as expected.

The induction period for isothermal decomposition of the "dry" peroxide (and hence for explosion) is determined predominantly by the rate of decomposition in the solid phase, for which the apparent activation energy, under conditions favouring conservation of the condensed products, has been found to be 56,500 cal/mole⁸. The slope of the line for the induction periods in Fig. 3 corresponds to an activation energy of 58,000 cal/mole and thus agrees reasonably well with the above.

Induction periods for explosion of the benzoyl peroxide paste are also plotted in Fig. 3 and, at a given temperature, are seen to be much shorter than for the "dry" peroxide (these were measured, more conventionally, as the time to the inflexion in the temperature record prior to the explosion (Fig. 2)). The results lie about a line of slope corresponding to an activation energy of 43,000 cal/mole, which is comparable with the value obtained from the explosion data for the paste, i.e. 44,800 cal/mole.

Fourier numbers, $\lambda t_i / \rho c r^2$, calculated from the induction periods for explosion of the peroxide paste for each size of charge, and using constants appropriate to the unreacted paste (Appendix), lie within the range 3.4 ± 0.1 . These values are markedly higher than the value of about 0.5 which would be expected, on the basis of the computations of Zinn and Mader²⁴, for ambient temperatures of, say, 0.5 degC, in excess of the ideal critical values. Part, but by no means the whole, of the excess may be due to the ratio λ/ρ (applicable, strictly, only to the unreacted paste) being somewhat high (as already noted).

DISCUSSION

It has been convenient above to make detailed comments as required in the course of the presentation and analysis of the results. There remain, however, two topics of general interest which require further discussion. These are the effects of the melting and mixing of the charge during self-heating and explosion, and conclusions with regard to the assessment of the practical hazard of thermal explosion.

Melting and Mixing effects

From an inspection of tabulated values²⁵ for the latent heats of fusion of organic compounds it is to be expected that the heat absorption accompanying the melting of the decomposing peroxide will be of the order of 10 per cent of the heat of decomposition and will not, therefore, greatly affect the critical conditions for explosion. The most important consequence of melting appears to be the opportunity thus provided for mixing of the charge by the evolved gas. The effects of this mixing are here rather less pronounced than observed by Merzhanov et al during the thermal explosion of molten tetryl⁵ when, for example, the sub-critical temperature rise was up to five times the expected value.

A useful starting point for discussion of the effects of mixing noted in this paper, is to view mixing as a transition from generalised "Frank-Kamenetskii" to "Semenov" conditions, as follows.

Replacing β by α (i.e. hr/λ) in equation (5) and putting $\mathcal{S} = \mathcal{S}_c$ when $\theta_0 = 1$, we have

$$\mathcal{S}_c = \frac{2}{e} \frac{L+r}{L} \alpha \quad (13)$$

For small values of α ¹⁶, this equation represents the critical condition for the "Semenov" case for thermal explosion in the short cylinder, i.e. for zero temperature gradient throughout the cylinder, and in the absence of mixing. If, however, the charge is mixed by artificial stirring, or by vigorous gas evolution, the above equation can represent the critical conditions for all values of α (the λ in α being the thermal conductivity of the undisturbed charge). It will be convenient, from this point onwards to denote the critical value of \mathcal{S} for the Semenov case as $\mathcal{S}_c(S)$.

Again replacing β by α in equation (5) and dividing by equation (13), the following equation is obtained for the sub-critical steady states of the stirred system (in the $\mathcal{S}(S)$ notation):-

$$\frac{\mathcal{S}(S)}{\mathcal{S}_c(S)} = \theta_0 e^{1-\theta_0} \quad (14)$$

For $\mathcal{S}(S) / \mathcal{S}_c(S) < 1$, equation (14) is satisfied by two sets of values of θ_0 ; those in the range $0 \leq \theta_0 \leq 1$ correspond to the stable sub-critical steady states, and those for $\theta_0 > 1$ the unstable steady states, of the well known qualitative picture of thermal explosion^{1, 2}.

Introducing a similar notation for the general Frank-Kamenetskii case, let $\mathcal{S}_c(F-K)$ represent a slightly super-critical value of \mathcal{S} for an initially unmixed self-heating system (short cylinder). Now at any given α ,

$\mathcal{S}_c(F-K) < \mathcal{S}_c(S)$ ¹⁶ and, if at some stage of the heating, mixing through gas evolution occurs to an extent sufficient to convert the system to the "Semenov" condition, $\mathcal{S}_c(F-K)$ will represent a sub-critical value of $\mathcal{S}(S)$ (at the given α) and the system will cool down unless the value of θ_0 after mixing exceeds the upper value of θ_0 in

$$\frac{\mathcal{S}_c(F-K)}{\mathcal{S}_c(S)} = \theta_0 e^{1-\theta_0} \quad (15)$$

If θ_0 is greater than the upper solution, the temperature will continue to rise to explosion following the temporary fall due to the mixing. Equation (15) thus defines the condition for the quenching of an incipient explosion by a mixing process.

In general, the critical value of δ (at given α) necessary for explosion of a self-mixing system must exceed δ_c (F-K) calculated for the unmixed system, and the earlier mixing occurs during the self-heating, the nearer will the required value of δ be to δ_c (S) at the given value of α . Thus, while equation (15) defines the maximum possible value of the temperature rise after mixing that can be followed by quenching of the explosion; in practice it will usually be less.

Values of the limiting temperature rise, θ_0 , for quenching ("quenching temperature"), calculated for the peroxide paste, are given in Table 5; they are based on δ_c (S) = 0.96 α for L/D = 1.6. Also tabulated, are the minimum values of the temperature rise at the moment of complete mixing observed for charges which exploded, expressed in terms of θ_0 (note that when $\theta_0 = 1$, $T_0 - T_A \doteq 5$ degC).

Table 5
Quenching temperatures for peroxide paste

Charge diameter cm	α	$\frac{\delta_c \text{ (F-K)}}{\delta_c \text{ (S)}}$	Quenching temperature θ_0	Temperature at mixing θ_0
2.7	3.4	0.40	3.1	2.0
4.1	3.2	0.32	3.4	3.0
5.0	3.5	0.38	3.1	3.5
8.0	4.3	0.34	3.3	5.0

The temperature rise after mixing increases as the size of sample increases, which is consistent with mixing occurring at a later state in the self-heating of the larger sizes than in the smaller sizes at higher ambient temperatures; in the larger sizes, the temperature rise exceeds the maximum quenching temperature by a considerable margin. For the smallest size the temperature rise after mixing is represented by $\theta_0 = 2$ and, if the actual quenching temperature is not to exceed this value, the actual critical value of δ for explosion must exceed δ_c (F-K) calculated for the undisturbed system by at least 75 per cent - which is equivalent to an ambient temperature exceeding the value required by the Frank-Kamenetskii model by at least 3 degC.

Apart from the above, the mixing effect is so complex in detail that it can be discussed in no more than qualitative terms. Thus, it is clear from the temperature records for the paste, Fig. 2, that mixing started at the centre of a charge and spread relatively slowly to the outer surface. This is to be expected in view of the higher temperature at the centre, and especially when, as here, the decomposition reaction was accompanied by the melting of a solid which constituted a high proportion of the charge. The erratic record for the centre temperature for the sub-critical example in Fig. 2 suggests that melting and mixing was in progress for about 1 hour before the maximum was reached. This behaviour was quite general. A process of this kind opposing the temperature rise due to self-heating can clearly lead to higher sub-critical temperature maxima and longer induction periods than would be predicted theoretically for an immobile system. It is, in effect, equivalent to the progressive increase in heat transfer coefficient suggested by Mershanov et al.

The behaviour of the "dry" peroxide was even more complex (Fig. 1). The rise and fall of the centre temperature to give two maxima in the record for the sub-critical example occupied a period of about $\frac{1}{2}$ hour. At the mean temperature during this period, i.e. about 94°C , the half-life for the liquid phase decomposition is about 1 hour⁸, so reactant consumption will have been significant during the $\frac{1}{2}$ hour period. The observed behaviour becomes explicable if mixing at the centre of the sample occurred shortly before the maximum rate of decomposition was reached.

As an indication of the extent to which the driving force for mixing varied in these tests, it may be calculated that at the maximum rate of decomposition, and assuming carbon dioxide was produced at the rate of 1 mole per mole of peroxide decomposed²⁶, the average linear velocity of gas leaving the open surface of the charge increased by a factor of 10 from about 10^{-3} cm/sec for the largest charge of "dry" peroxide to 10^{-2} cm/sec for the smallest. This wide range, coupled with the initial acceleratory character of the decomposition of the dry peroxide, the progressive melting and the usual decrease of viscosity with temperature, implies that, at different temperatures, the mixing effect could become prominent at different stages relative to the maximum rate of decomposition. This seems the most plausible explanation for the considerable difference in slope of the explosion data and kinetic data for the "dry" peroxide in Fig. 3.

The decomposition of the molten tetryl studied by Merzhanov *et al.* was autocatalytic but was not complicated by melting. It may be noted that most of the ignition results obtained by these authors lie closely about a straight line of the expected slope (corresponding to $E = 38,000$ cal/mole) when plotted as in Fig. 3 of this paper; the main deviations occur with the smaller charge diameters.

Conclusions on hazard assessment

The practical objectives of this work have been to explore the suitability of the small-scale determination of critical conditions for thermal explosion as a method for assessing the risk of thermal explosion of unstable compounds during storage or transport. In particular, by studying the decomposition and thermal explosion of a typical unstable compound in sufficient detail, it was desired to determine the extent to which chemical or physical complexities might interfere with predictions based on the laboratory - scale observations.

The compound chosen for study, benzoyl peroxide, shows basically different decomposition patterns in the two forms employed, i.e. as a relatively pure solid and as a paste with plasticiser, and melting and mixing occurs as decomposition proceeds. Nevertheless, critical explosion data for the two forms are broadly consistent with one another and with the isothermal decomposition data when compared in terms of the generalised Frank-Kamenetskii model of thermal explosion.

In common with the observations of Merzhanov *et al.*, there is evidence that the effect of melting and mixing is to increase the critical temperature for ignition relative to that estimated to be required in the absence of mixing. For the "dry" peroxide this effect shows a pronounced systematic increase with temperature without, however, affecting the linearity of $\log (\delta_c T_A^2 / r^2)$ plotted against $1/T$.

The explosion data obtained do not cover a very large range of sizes and temperatures. Nevertheless, the linearity of the isothermal decomposition data for the paste in Fig. 3, indicates that an extensive linear extrapolation of the ignition data for the paste would be justifiable. For the "dry" peroxide, however, although the graph of the isothermal decomposition data (for the maximum rates) shows no indication of curvature in Fig. 3, it must eventually, at lower temperatures, curve downwards to have a slope appropriate to the purely solid phase reaction⁸. Critical sizes for thermal explosion of the "dry" peroxide, estimated for low temperatures by linear extrapolation of the ignition data will then tend to be too small but will err on the side of safety (at 60°C the estimated critical size may be about 50 per cent too small).

At low temperatures, the induction period for explosion of the "dry" peroxide will become very large indeed (e.g. about 8 months at 60°C). At higher temperatures, i.e. about 100°C and higher, the behaviour of pure benzoyl peroxide is different again; thus, studies of the isothermal decomposition by Morsi¹⁴, and of the thermal explosion by Fine and Gray²⁷, yield an activation energy of the order of 30,000 cal/mole - which is about half the value for the purely solid phase decomposition.

It is concluded that small-scale determinations of critical conditions for thermal explosion can, by linear extrapolation of the results plotted as in Fig. 3, provide a useful guide to the behaviour of unstable compounds under practical conditions. Reasonably reliable estimates of α are necessary but, otherwise, no direct measurements of physical properties are required. The method tends to be "self correcting" for the effects of melting and mixing by gas evolution and thus yields predictions which are more reliable than those based on a priori calculation from kinetic and calorimetric data using existing theoretical models for static systems. However, in order to reduce the extent of the extrapolation, the scale of the explosion tests should be as large as is compatible with convenience and safety.

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APPENDIX

PHYSICAL DATA

Values of the density and thermal conductivity for the peroxide materials in different states were obtained in a variety of ways. They are summarised in the following table and key.

Table

Material	State	Density g/cm ³	Thermal conductivity cal cm ⁻¹ s ⁻¹ degC ⁻¹
"Dry" benzoyl peroxide	compact solid	1.3 (a)	7 x 10 ⁻⁴ (c)
	granular solid	0.5 (b)	1.4 x 10 ⁻⁴ (d)
	molten	1.2 (e)	3.5 x 10 ⁻⁴ (c)
	molten "foam"	0.5	1.5 x 10 ⁻⁴ (d)
Benzoyl peroxide paste (35 per cent dimethyl phthalate)	mixture of solid and liquid	1.2 (b)	5.4 x 10 ⁻⁴ (d)

KEY

- (a) Published value²⁸
- (b) Observed
- (c) Estimated by comparison with published data for organic compounds of similar molecular weight and form (diphenyl and O-phenyl phenol) in solid and liquid states.²⁹
- (d) Estimated by means of Maxwell's equation for spheres dispersed in a continuous medium.²²
- (e) Estimated as 10 per cent less than density of solid.

The specific heat of the paste, required for calculation of the thermal diffusivity in the Fourier number, was chosen as 0.4 cal g⁻¹ degC⁻¹ from inspection of tabulated values for organic compounds²⁵ (c.f. 0.385 for diphenyl).

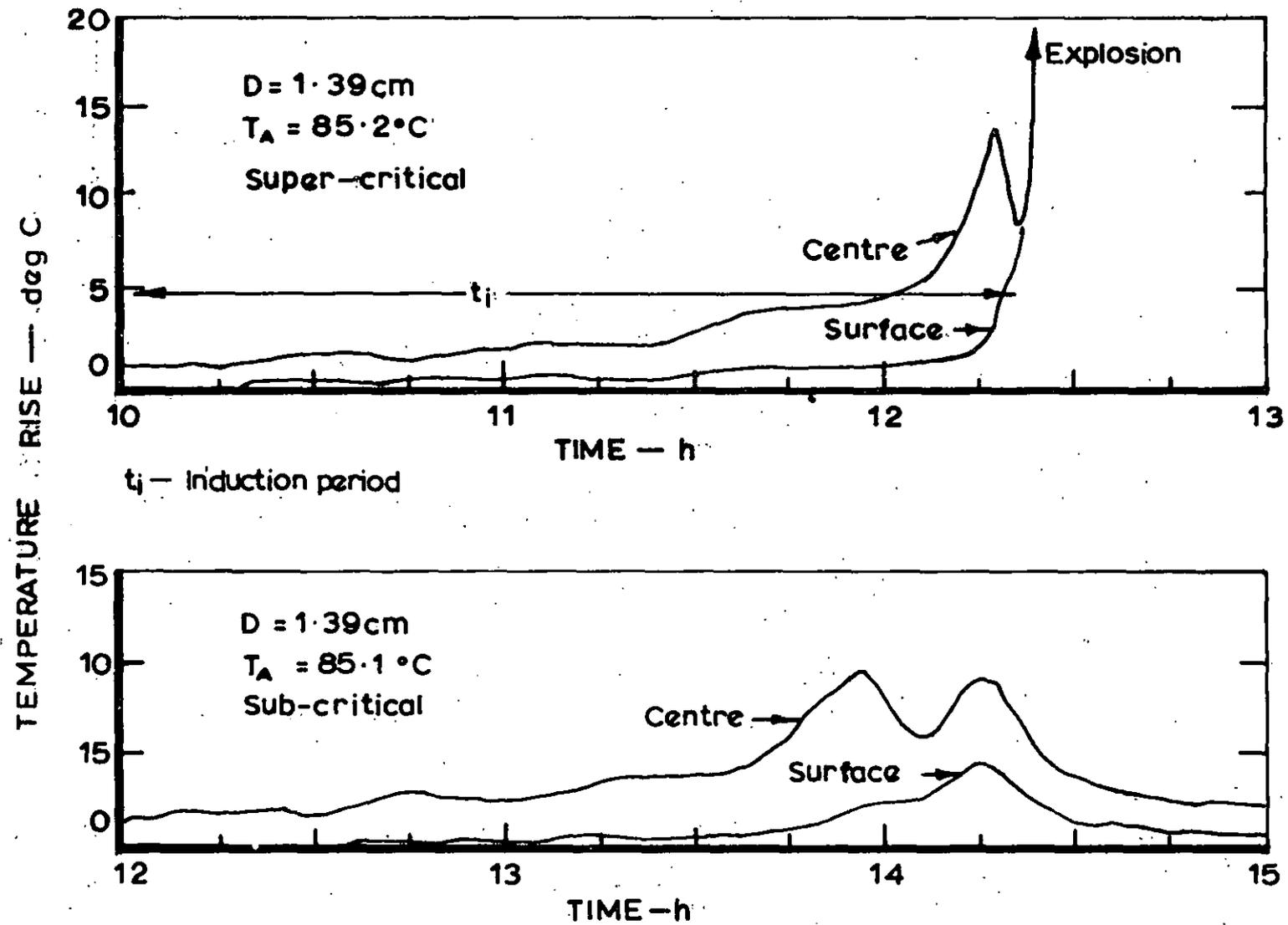


FIG.1. SELF-HEATING AND EXPLOSION OF 'DRY' BENZOYL PEROXIDE.

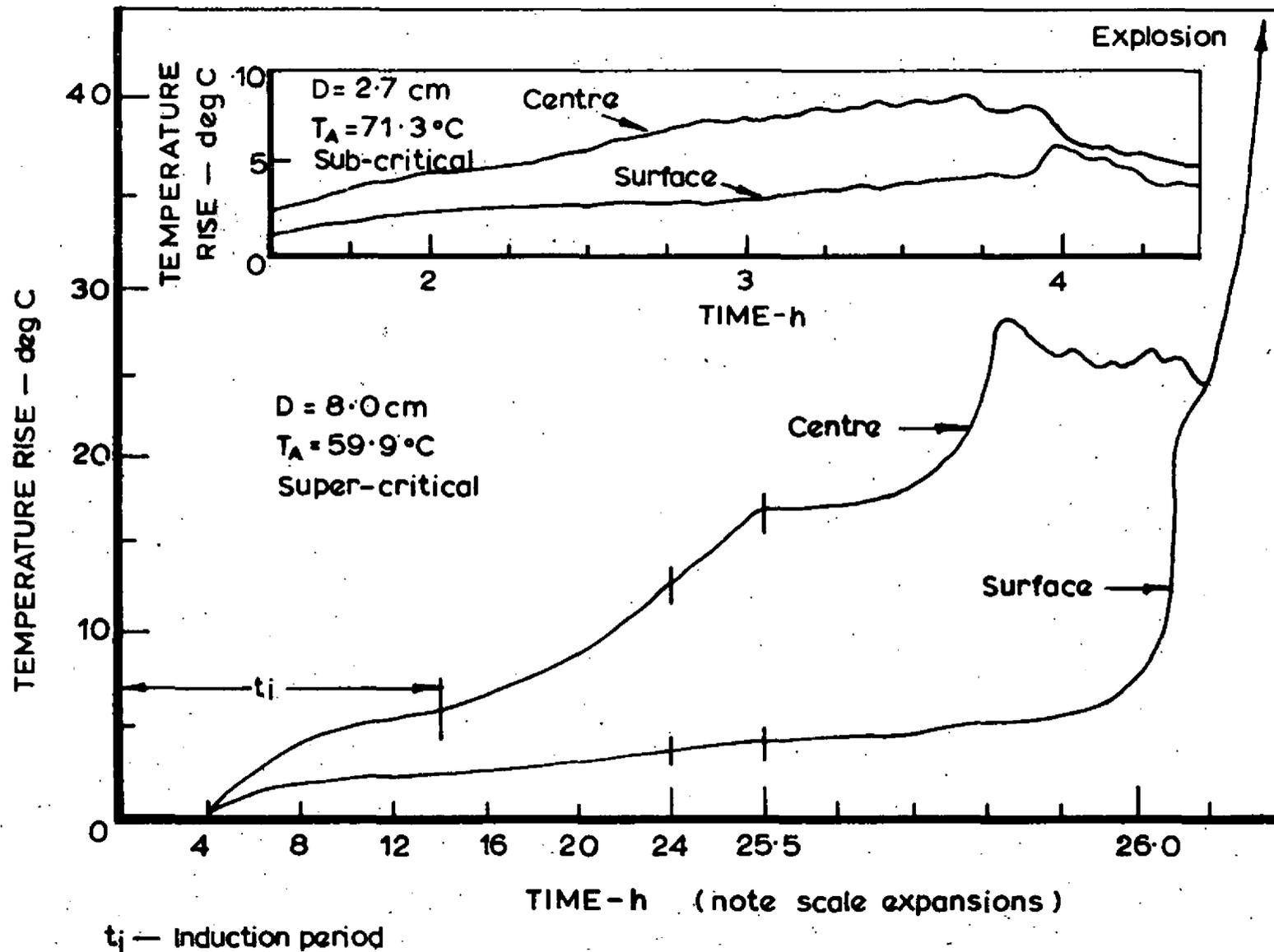


FIG.2. SELF HEATING AND EXPLOSION OF BENZOYL PEROXIDE PASTE

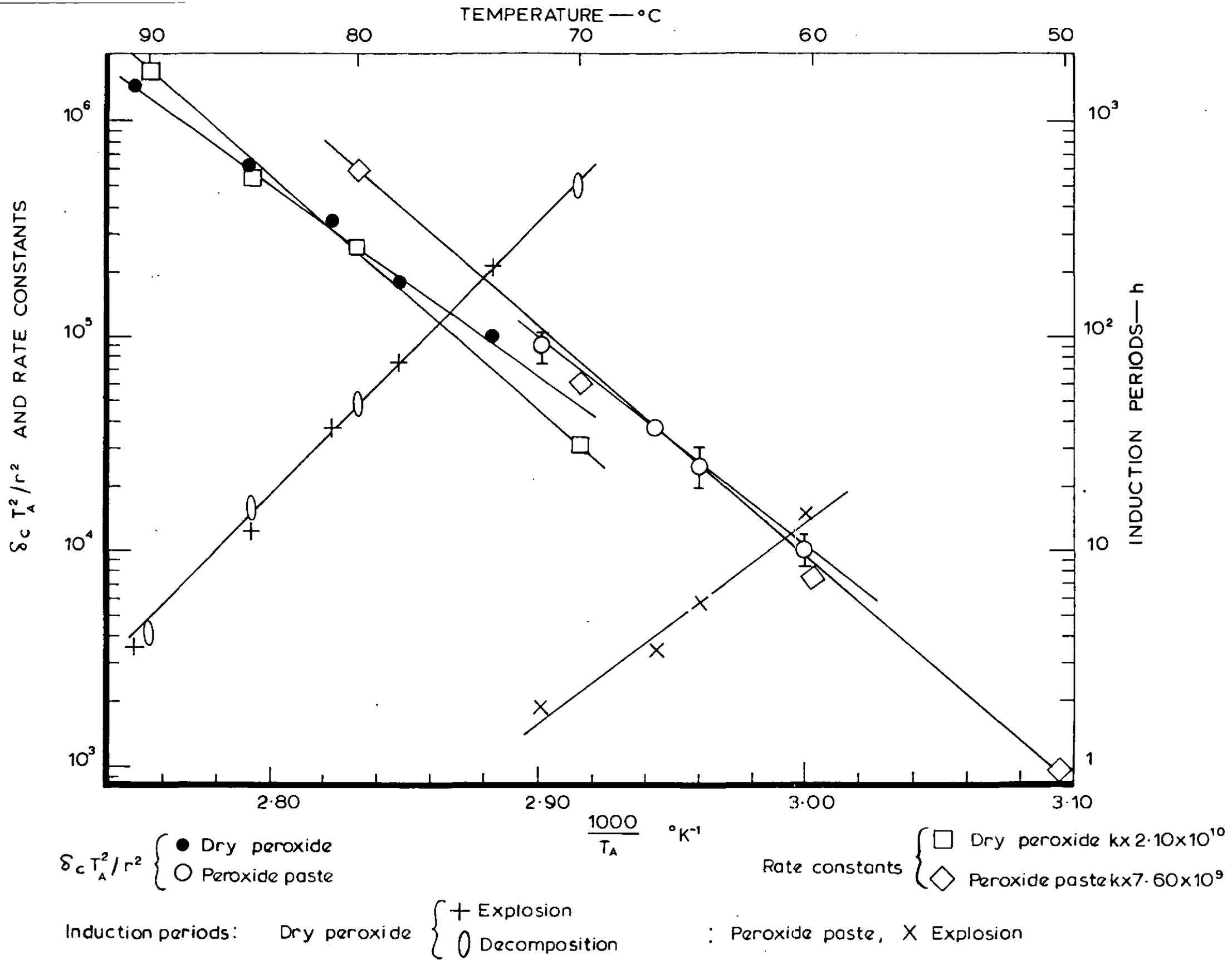


FIG.3. COMPARISON OF IGNITION AND KINETIC DATA

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v
v
v

v
v
v
v

o

