

LIBRARY REFERENCE ONLY

M.O.T. AND F.O.C. II
FIRE RESEARCH
ORGANIZATION
REFERENCE LIBRARY 69
No. A99FR. N 788



Fire Research Note No. 788

THE THERMAL EXPLOSION OF SOLID
UNSTABLE SUBSTANCES.

by

P. C. BOWES

October 1969

FIRE
RESEARCH
STATION

THE THERMAL EXPLOSION OF SOLID UNSTABLE SUBSTANCES

by

P. C. Bowes

ABSTRACT

e) The paper briefly reviews the thermal explosion model and summarises a study of the thermal decomposition and thermal explosion of some solid organic peroxides. The object of the study has been to consider the use of the Frank-Kament'skii model of thermal explosion for predicting safe conditions for storage and transport of unstable substances in general.

It is concluded that experimental determination of the critical ambient temperatures for the thermal explosion of small charges of given shape and size is likely to be the most flexible and reliable procedure for predicting large-scale behaviour with the aid of the theoretical model. But any procedure should be accompanied by, at least, a rudimentary exploration of the decomposition kinetics of the material under examination in order to detect the presence of factors likely to interfere with the extrapolation to full-scale.

KEY WORDS: Thermal explosion, organic peroxides, unstable substances.

Crown copyright

This report has not been published and should be considered as confidential advance information. No reference should be made to it in any publication without the written consent of the Director of Fire Research.

THE THERMAL EXPLOSION OF SOLID UNSTABLE SUBSTANCES

by

P. C. Bowes

INTRODUCTION

As an approach to the problem of defining the risk of thermal explosion in the storage and transport of substances and mixtures which are chemically unstable at temperatures in the neighbourhood of ordinary atmospheric temperatures, studies have been made of the thermal decomposition and thermal explosion of some solid organic peroxides. The results of these studies have been given in detail in a series of Fire Research Notes¹⁻⁷ and elsewhere⁸.

The purpose of the present paper is to place the above work in a wider perspective and to consider the general implications for the practical problem of hazard assessment more fully than has been possible hitherto.

A direct assessment of the risk of thermal explosion, consisting of a determination of minimum temperatures for self-accelerating decomposition on full-sized packages of material is sometimes possible⁹. However, it is not to be expected that this approach will always be possible, or even desirable, and hazard assessment is likely to continue in most cases to be based on small-scale tests whose interpretation in terms of the full-scale must rest either on experience or on a theoretical model.

A theoretical model is available for the phenomenon of thermal explosion which is becoming well established. It has been shown, by Merzhanov and his associates especially¹⁰⁻¹³, that under sufficiently well-defined conditions, the model is applicable quantitatively to the thermal explosion of a number of condensed substances (principally explosives) in different environments. It also finds application to the self-heating and ignition of cellulosic materials¹⁴.

The question at issue in the context of this paper, is the extent to which the model is likely to be generally applicable to practical cases. This extent will depend on (a) limitations inherent in the model (b) the mode of application of the model (principally as governed by the experimental procedures selected), and (c) complexities in real systems for which the model may be unable to cater. Each of these aspects will be considered here.

THEORETICAL MODEL

Extended accounts of the theory of thermal explosion^{15,16}, and of the rapid developments of the last decade or so, are available in recent reviews^{17,18}. Here it is sufficient to state briefly the relevant results. Principally, these derive from the "steady state" analysis¹⁶ of thermal explosion in an environment at constant uniform temperature.

Given a body of material, in the above environment, generating heat by a reaction which is of "zero order", and whose rate varies with temperature in accordance with the Arrhenius equation, the body will undergo thermal explosion when the value of a parameter, δ , defined by equation (1) below, exceeds a certain critical value, δ_c .

$$\delta = \frac{E}{RT_A^2} \cdot \frac{\rho r^2}{K} \cdot Q A e^{-E/RT_A} \quad (1)$$

where A = pre-exponential factor in Arrhenius equation
 E = activation energy
 K = thermal conductivity
 Q = heat of reaction per unit mass
 r = linear dimension of body (thickness of slab, radius of infinite cylinder or sphere)
 R = universal gas constant
 T_A = ambient temperature
 ρ = density of body.

The critical value, δ_c , depends on the geometry of the body and on the boundary conditions. For a finite value of the surface heat transfer coefficient, h, δ_c has been calculated as a function of α , where $\alpha = hr/K$, for different centrosymmetric geometries by approximate analytical or numerical procedures from the governing equations of the model^{7,17-20}. When $\alpha \rightarrow 0$,

$$\delta_c = \frac{(1+p)}{e} \frac{hr}{K} \quad (2)$$

(where p = 0, 1, 2 for slab, infinite cylinder, sphere respectively) which corresponds to the Semenov model¹⁵ based on the assumption of uniform temperature throughout the body (K effectively infinite). When $\alpha \rightarrow \infty$, we have the Frank-Kamenetskii model¹⁶ for a body of finite thermal conductivity and constant surface temperature equal to T_A (h effectively infinite).

When $\delta < \delta_c$, a relatively small steady state temperature increase becomes established in the body. The central, maximum, value is given by

$$\theta_0 = \frac{E}{RT_A^2} (T_0 - T_A) \quad (3)$$

where T_0 is the central temperature. θ_0 has an upper limit when $\delta = \delta_c$ which is dependent on the geometry of the body and the boundary conditions.

When the rate of reaction (and heat evolution) is dependent on the extent of the reaction, i.e. the reaction is not of zero order, no steady states are possible. θ_0 then has maxima with respect to time which increase continuously as δ increases. The character of the "explosion" then depends on the magnitude of the adiabatic temperature increase for the system B (dimensionless) given by

$$B = \frac{E}{RT_A^2} \frac{Q}{C} \quad (4)$$

(where C = specific heat of body).

Provided B is sufficiently large (of order 10 or more) maximum values of θ_0 increase from low values (similar in magnitude to those characteristic of steady states for zero order reactions) to high values over a small range of increase in δ , i.e. a relatively sharply defined explosion occurs.

Computer solutions²¹ for the temperature increase in an infinite cylinder, with $B = 100$ and $\alpha = 2$, show that θ_0 increases from a maximum of 1.4 to high values for an increase in δ of about 1.6 per cent. This corresponds to an increase in the size of a body, at a given ambient temperature, of about 0.8 per cent or, for $T_A \sim 300^\circ\text{K}$ and $E = 30,000$ cal/mole, to an increase in ambient temperature of about 0.1°C . Thermal explosion as sharply defined as this may be expected for unstable substances for which heats of decomposition are of order 10^2 cal/g - which is not unusual.

When a finite loss of reactant occurs by a reaction of n^{th} order during the self-heating prior to explosion, the appropriate value of the critical parameter δ_c is given by

$$\delta_c (B/n) = \delta_c (\infty) \left[1 - 2.52 \left(\frac{n}{B} \right)^{\frac{2}{3}} \right]^{-1} \quad (5)$$

where $\delta_c (\infty)$ is the value appropriate to zero order reaction, the coefficient 2.52 being the value recently suggested by Gray and Lee²². For a first order

reaction ($n = 1$), a value of 100 for B increases $\delta_c(\infty)$ by 13 per cent; for $B = 20$, the increase is about 50 per cent.

The various approximate procedures available for estimating the critical values of δ for different geometries and boundary conditions may introduce errors of up to about 10 per cent - exceptionally 15 per cent - of more exact computer solutions¹⁷. An error in δ_c of 10 per cent will introduce an error of 5 per cent in estimates of critical size, or an error in estimates of critical ambient temperature which, for realistic values of E and T_A , may be 1-3 degC. Errors of this magnitude in the absolute value of δ_c will be of little practical significance.

The cardinal requirement in applications of the model is that the temperature dependence of the rate of heat evolution shall obey the Arrhenius equation sufficiently well over the temperature range of interest. This will be pursued further below.

The theoretical model also yields estimates of induction periods for thermal explosion¹⁵⁻¹⁸. These will not, however, be discussed here. In this paper we shall be concerned more with the effect of induction periods in the reactions responsible for heat generation.

These may overshadow the "thermal" induction periods and it will be seen that they can limit the usefulness of certain of the experimental procedures.

EXPERIMENTAL PROCEDURES

Experimental procedures for assessing the thermal explosion hazard may be summarised briefly as follows:

Empirical procedures

Although not capable of providing quantitative guidance on safety of transport and storage, determinations of "minimum temperatures" for exothermic decomposition, based on the exposure of small samples of material to fixed elevated temperatures, or to rising temperatures, are commonly used and are of obvious value for detecting tendencies to thermal explosion (for example, with special reference to organic peroxides, see Manly²³, Siemens²⁴ and Noller and Bolton²⁵). Tests such as these take no cognisance of critical size but can indicate broadly whether further, more quantitative, investigation is desirable; they may, however, give somewhat misleading indications of hazard (see further).

Basic procedure

This implies separate determination of all the physical and chemical constants required for calculating critical conditions for thermal explosion using the equations of the model. This is, of course, the appropriate procedure in initial checks of the validity of the theoretical model and, naturally, makes maximum demands on the exactness of the model. It is unlikely to be the most convenient in routine practical applications.

Calorimetric procedures

These consist of determining the rate of heat evolution as a function of time and temperature. The determination may be by adiabatic calorimetry (Gross and Amster²⁶), isothermal heat flow calorimetry (van Geel²⁷) or D.T.A. (e.g. by Bohon²⁸ for explosives).

Extraction of the data needed for use in the thermal explosion model, from the calorimetric results, may require simplifying assumptions to be made about the reaction kinetics. Incorrectness in these assumptions at this stage may introduce important errors.

Separate determination of physical constants are needed.

Simulatory procedure

This consists of carrying out small-scale explosion experiments and extrapolating the results to full-scale with the aid of a theoretical relationship.

The appropriate relationship for thermal explosion with an Arrhenius type temperature dependence for reaction rate is obtained by rearrangement of equation (1) to give

$$\ln (\delta_c T_A^2/r^2) = -\frac{E}{RT_A} + \text{constant} \quad (6)$$

where T_A is the critical ambient temperature for explosion of charge of characteristic dimension r and δ_c is the calculated critical value of δ_c appropriate to the geometry and surface heat-transfer parameter α .

A minimum of two (though preferably more) experimental results for different sizes, and estimates of δ_c , suffice for linear extrapolation subject to the requirement that the Arrhenius equation is obeyed sufficiently well.

This is the approach that has been used in the study of thermal explosion in organic peroxide preparations reported briefly below.

THERMAL EXPLOSION OF ORGANIC PEROXIDES

Critical ambient temperatures for thermal explosion were determined for two preparations of benzoyl peroxide in open-topped cylindrical containers. These preparations consisted of the pure (98 per cent) granular solid and a paste containing 65 per cent benzoyl peroxide and 35 per cent dimethyl phthalate. The isothermal decomposition of the preparation at different temperatures was also studied in order to determine the appropriate kinetic constants.

The course of the isothermal decomposition was different for the two peroxide preparations. The pure peroxide showed the sigmoid decomposition/time relationship common to many organic solids. The acceleratory stage was associated with the accumulation of a liquid phase in which the decomposition of the peroxide was faster than in the solid phase, the rate reaching a maximum near the point of complete liquefaction¹. The extent of the decomposition at which complete liquefaction occurred became greater as the temperature was reduced. The "induction period", i.e. the time to the maximum rate of decomposition, increased rapidly as the temperature was reduced; at 70°C it was as long as 800 hours.

Another solid peroxide studied, lauroyl peroxide⁶, showed similar behaviour to that of the pure benzoyl peroxide although the early stage of the solid phase decomposition was more complex.

The decomposition of the benzoyl peroxide paste, on the other hand, followed a simple course. The initial rate, which was relatively high, remained constant for up to 40-60 per cent decomposition (depending on the temperature) and then decayed.

In accordance with the model for thermal explosion in "autocatalytic" systems¹⁶⁻¹⁸, critical conditions for thermal explosion of the pure benzoyl peroxide were assumed to be determined by the maximum rates of decomposition, these maximum rates, at different temperatures, being treated as rate constants for a hypothetical "zero order" reaction. For the paste, the appropriate constants were determined from the initial rates.

The quantitative results for the benzoyl peroxide are summarised in Fig.1 (reproduced from refs 3 and 8) where the critical explosion results^{3,8} are plotted in accordance with equation (6) and are compared with the rate constants for isothermal decomposition. For the purpose of calculating δ_c , values of α were estimated from temperatures measured at the centre and surface of the charges, and the ambient (furnace) temperatures^{7,8}. The cylindrical charges, with a height to diameter ratio of 1.6, ranged in diameter from 0.86 to 3.72 cm for the pure

peroxide and 2.7 to 8.0 cm for the paste.

The features to be noticed in Fig.1 may be listed as follows:-

1. The explosion results plotted in accordance with equation (4) are linear as required, which implies that the Arrhenius equation is obeyed at least over the temperature range covered.
2. The graphs of the rate constants are also linear as required by the Arrhenius equation, but there is a small difference in slope between these lines and those for the explosion results. The activation energies calculated from the gradient of the rate constants in Fig.1 are 50,500 cal/mole for the pure peroxide and 49,300 cal/mole for the paste. Values obtained from the explosion data are 40,800 cal/mole for the pure peroxide and 44,800 cal/mole for the paste. It is important to note that these values are considerably higher than the value of about 30,000 cal/mole obtained for decomposition of the pure peroxide at temperatures near and above its melting point^{29,30} and in solution³¹.
3. The factors multiplying the rate constants in Fig.1, chosen to make the kinetic data and explosion data intersect at about the middle of their ranges, may be used to calculate the heat of decomposition of the peroxide from equation (1) (given \int_c)³. The values obtained from this source, and also from self-heating data³, lie in the range 255 ± 50 cal/g - which is comparable with the range expected on thermochemical grounds, i.e. 263 ± 40 cal/g²⁹.
4. The comparison of the induction periods for the decomposition and explosion of the pure peroxide confirms that explosion is closely associated with the maximum rate of isothermal decomposition.

The differences in slope for the explosion data and kinetic data in Fig.1 are attributable to melting and mixing (associated with gas evolution) of the charges prior to explosion^{3,8}. This mixing effect, which can quench an incipient explosion, necessitates a higher ambient temperature for explosion than that predicted by the Frank-Kamenetskii model. It can be argued that the required excess depends on the temperature⁸. Apart from this complicating factor, there is reasonable quantitative agreement with the model in the range of sizes covered experimentally.

The linearity of the graph of rate constants for the paste in Fig.1 down to 50°C, implies that the explosion data for the paste may be extrapolated at least as far as this.

However, this is not so for the pure peroxide. Although the graphs of the explosion data and rate constants show no sign of curvature in Fig.1, they must eventually, at lower temperatures, attain a steeper downward slope appropriate to the much slower solid phase reaction¹. Critical sizes for thermal explosion at lower temperatures, estimated by linear extrapolation of the available explosion data, will therefore tend to be too small (thus erring on the side of safety). Again, because the maximum rate of decomposition occurs at greater degrees of decomposition as the temperature is reduced, there will eventually be no explosion. A correction for this effect could be applied to the critical value of δ by using equation (5) and values of the residual heat of reaction in B (equation (4)) appropriate to the degree of decomposition for each experimental point (the decay in reaction rate following the maximum is first order¹). The effect of this correction will be slightly to increase the difference in slope for the explosion data and rate constants for the pure peroxide.

For both these reasons, only a limited downward extrapolation of the explosion data for the pure peroxide is meaningful. It has been estimated⁸ that extrapolation to 60°C will yield a critical size which is about 50 per cent too small. At this temperature, the predicted induction period for thermal explosion of the pure peroxide is very large, about 8 months.

Neglecting the small differences in apparent activation energy, and estimating a possible heat of decomposition for lauroyl peroxide from bond energies⁶, it may be estimated that critical sizes for thermal explosion of the three organic peroxide preparations studied will have the following relative magnitudes at a given temperature (< 60°C).

Lauroyl peroxide	1
Benzoyl peroxide paste	6
Benzoyl peroxide, pure	12

An interesting feature of this comparison is that lauroyl peroxide, which is relatively insensitive and safe to handle, is the most hazardous from the point of view of critical size for thermal explosion. At 40°C for example, the estimated critical diameter ~~estimated~~ for a cylindrical package is 21 cm; even if the value used for the heat of reaction (196 cal/g) is too large by a factor of 2, this size will be increased by only about 40 per cent. However, induction periods for decomposition of lauroyl peroxide at temperatures below its initial melting point increase even more rapidly as the temperature is reduced than those for pure benzoyl peroxide. The extrapolated value for lauroyl peroxide at 40°C is 5½ years. For reasons indicated above the relative critical diameter for pure benzoyl peroxide is likely to be considerably greater than 12 at temperatures such as this.

DISCUSSION

Broadly speaking, the thermal explosion behaviour of the two preparations of benzoyl peroxide studied is in quantitative agreement with the theoretical model and, in this respect, is consistent with that of other condensed substances¹⁰⁻¹³. The detailed behaviour, however, exemplifies a number of features (also observed in different degrees in other substances) which can affect the value of the different procedures available for estimating the practical hazard.

At the empirical level, it may be noted that where long induction periods exist, such as have been observed for the pure benzoyl and lauroyl peroxides, determinations of "minimum temperatures" for exothermic decomposition may fail to reveal the possibility of thermal explosion at temperatures below the melting points of solids. Also the effect of additives which merely reduce induction periods may be misinterpreted as an increase in the tendency to explode.

For the same reason that a high heat of reaction enables reactant consumption to be ignored in the thermal explosion model (i.e. the higher the heat of reaction, the smaller the reactant consumption necessary to produce a given temperature increment), a high heat of reaction should ensure that the adiabatic procedure of Gross and Amster²⁶ yields valid estimates of rates of heat evolution and activation energies for simple decomposition reactions. For autocatalytic types of reaction however, it is probable that, with a high heat of reaction, only some early stage of the reaction would yield a temperature/time curve from which measurements of slope could be made.

There appears to be no interpretative scheme available for obtaining kinetic constants for autocatalytic type reactions from D.T.A. records, but this procedure is capable of providing kinetic constant for simpler reactions³².

Of the calorimetric procedures, isothermal heat-flow calorimetry²⁶ at different temperatures should furnish satisfactory values for rates of heat evolution and activation energy for reactions at least as complicated as that observed for the pure benzoyl peroxide - given the long term stability required by the large induction periods.

Even when reliable kinetic constants are available for the heat generation, however, estimates of critical conditions for explosion based on existing models can make no allowance for the effect of factors such as melting and mixing of the charge by gas evolution. It is in this respect that the simulatory procedure shows more flexibility than other procedures. Here, the effect has systematically modified critical explosion temperatures for the pure benzoyl peroxide and so

affected the slope of the linear data plot (Fig.1). As has been pointed out elsewhere⁸, the decomposition of molten tetryl studied by Merzhanov et al¹³ was autocatalytic but not associated with progressive melting, and, while mixing effects led to deviation from expected critical temperatures, explosion data plotted in accordance with equation (6) was linear and had the gradient expected from kinetic data.

The principal obstruction to extrapolation of the explosion data is a major change in chemical and physical factors controlling the overall reaction. Here it has been seen that reaction kinetics for decomposition of the pure benzoyl peroxide at temperatures above its melting point are different from those below the melting point. Again, in the direction of lower temperatures, there must be a change to kinetics characteristic of purely solid phase reactions. In general, therefore, it appears that, whatever procedure is adopted for predicting thermal explosion hazard, it should always be accompanied by, at least, a rudimentary exploration of decomposition behaviour over a large range of temperature; this should indicate the presence of factors likely to interfere with the extrapolation.

Substances which have so far been examined in any detail in the present context have been single substances with relatively simple overall exothermic decomposition kinetics. It is possible for mixtures, e.g. propellants, to show complex exotherms²⁶ suggesting the presence of independent reaction which may proceed in parallel or consecutively. This may occasionally pose major problems in the prediction of explosion behaviour, especially from calorimetric data.

An analysis of self-heating and ignition data for wood-fibre insulating board¹⁴ has shown that the presence of a minor short-lived exothermic reaction can have a major effect on sub-critical self-heating without however affecting the linearity of ignition data plotted in accordance with equation (6). To this extent, therefore, the simulatory procedure can avoid difficulties from this source; in effect, determinations of critical temperatures for explosion, select the reaction important for explosion. A recent theoretical analysis³³ of a simple self-heating system of two components reacting independently has indicated quantitatively how this can happen for certain ranges of the relevant parameters (exemplified by the wood-fibre insulating board). However there are other ranges where the representation of explosion data in terms of equation (6) alone will not be sufficiently linear to permit extrapolation. This more elaborate model has yet to be tested for unstable substances, although it has been applied with success to the self-ignition of mixtures of sawdust and vegetable oil³⁴.

Although this paper has been concerned with solid materials, it has some relevance to thermal explosion in liquid systems where perhaps the Semenov model may find greater application. However, further complications arise in liquid systems, for example the occurrence of explosion may be controlled by pressures generated during vapour boil-off^{35,36}. In general, the thermal explosion of liquids does not appear to have been sufficiently widely studied for one to feel confident that the thermal model is always applicable.

CONCLUSION

The experimental determination of critical ambient temperatures for the thermal explosion of small charges of given shape and size is likely to be the most flexible and reliable procedure for predicting large-scale behaviour in the storage and transport of unstable substances on the basis of the theoretical model of thermal explosion. Any such procedure, however, should be accompanied by, at least, a rudimentary exploration of the decomposition kinetics of the material under examination.

REFERENCES

Fire Research Notes of the Ministry of Technology and Fire Offices' Committee Joint Fire Research Organization:-

1. BOWES, P. C. The thermal decomposition of benzoyl peroxide in the solid state. Fire Research Note No.571, 1964.
2. Idem. The thermal decomposition of benzoyl peroxide pastes. Fire Research Note No.616, 1966.
3. Idem. Thermal explosion of benzoyl peroxide. Fire Research Note No.650, 1967.
4. Idem. Thermal explosion of unstable compounds. Experimental equipment and methods. Fire Research Note No.626, 1967.
5. BOWES, P. C. and RAFTERY, M. M. The effect of impurities on the thermal decomposition and explosion, and sensitivity, of benzoyl peroxide. Fire Research Note No.677, 1967.
6. BOWES, P. C. and HARRIS, J. Thermal decomposition of lauroyl peroxide. Fire Research Note No.684, 1967.
7. BOWES, P. C. Thermal explosion in the short cylinder with a general boundary condition. Fire Research Note No.642, 1966.

Other sources (some original sources given in the books and reviews, 15-18, are not repeated in this paper):-

8. BOWES, P. C. Combustion and Flame 1968, 12, 289.
9. NOLLER, D. G. et al. Industr. Engng. Chem. (~~Indust. Engng. Chem.~~) 1964, 56 (12) 19.

10. MERZHANOV, A. G. Combustion and Flame 1967, 11 (3), 201.
11. MERZHANOV, A. G., BARZYKIN, V. V., ABRAMOV, V. G. and DUBOVITSKII, F. I. J. Phys Chem. USSR (transln) 1961, 35, 1024.
12. BARZYKIN, V. V. and MERZHANOV, A. G. J. Phys Chem. USSR (transln) 1964; 38, 1431.
13. MERZHANOV, A. G., ABRAMOV, V. G. and DUBOVITSKII, F. I. Dokl. Akad. Nauk. SSSR 1959, 128, 1238.
14. THOMAS, P. H. and BOWES, P. C. Brit. ~~J~~ Appl. Phys 1961, 12, 222.
15. SEMENOV, N. N. Some problems of chemical kinetics and reactivity Vol.II. Pergamon : London (1959).
16. FRANK-KAMENETSKII, D. A. Diffusion and heat exchange in chemical kinetics. Translated by N. Thon. Princeton University Press, Princeton (1955).
17. MERZHANOV, A. G. and DUBOVITSKII, F. I. Russian Chemical Reviews 1966, 35 (4) 278.
18. GRAY, P. and LEE, P. R. Thermal explosion theory. Oxidation and Combustion Reviews. Vol.2 1967. Elsevier Publishing Co. London.
19. THOMAS, P. H. Trans Faraday Soc. 1958, 54 (1) 60.
20. THOMAS, P. H. Ibid 1960, 56 (6) 833.
21. BARZYKIN, V. V., GONTKOVSKAYA, V. T., MERZHANOV, A. G. and KHUDYAEV, S. I. Zh. Prik. Mekh i Tekh. Fiz., 1964, 3 118.
22. GRAY, P. and LEE, P. R. Combustion and Flame 1965, 9, 202.
23. MANLY, T. D. Industr. Chem. Mfr. 1956, 32, 319.
24. SIEMENS, A. M. E. British Plastics 1962, 35, (7), 357.
25. NOLLER, D. C. and BOLTON, D. J. Analyt. Chem. 1963, 35 (7), 887.
26. GROSS, D. and AMSTER, A. B. Eighth Symposium (International) on Combustion. The Williams and Wilkins Company, Baltimore 1962, p.728.
27. GEEL, J. L. C. van, Industr. Eng. Chem., 1966 58 (1) 24.
28. BOHON, R. L. U.S. Analyt. Chem., 1963, 35 (12), 1845.
29. FINE, D. and GRAY, P. Combustion and Flame 1967, 11, 71.
30. MORSI, S. El-Din. The thermal decomposition of organic per-compounds. Thesis, University of London, 1964.
31. TOBOLSKY, A. V. and MESROBIAN, R. B. Organic peroxides. Interscience, London, 1954.
32. REED, R. L., WEBER, L. and GOTTFRIED, B. S. Industr. & Engng Chem., 1965, 4 (1) 38.

33. BOWES, P. C. In the press. (Combustion and Flame).
34. Fire Research 1968, H.M.S.O. 1969. To be published in detail elsewhere.
35. DRIVER, R. M. Trans. Faraday Soc., 1967, 63, 974.
36. RUTLEDGE, P. V. Chem. and Ind. 1967, 34.

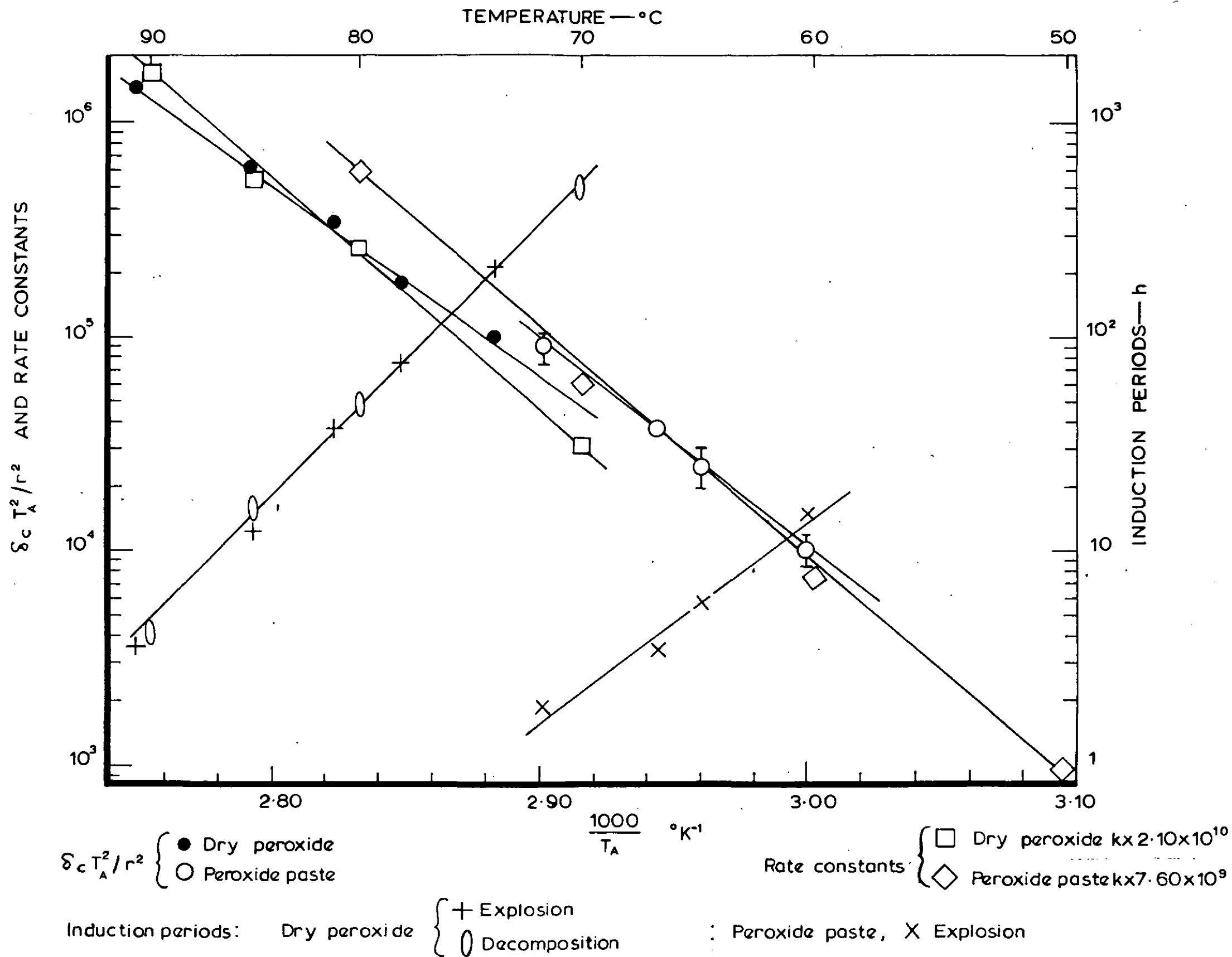


FIG.1. COMPARISON OF IGNITION AND KINETIC DATA

