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THE THERMAL DECOMPOSITION OF BENZOYL
PEROXIDE IN THE SOLID STATE

by

P. C. BOWES

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SUMMARY

The thermal decomposition of benzoyl peroxide of 98 per cent purity has been studied, at atmospheric pressure, at a series of temperatures between 70 and 95°C. A liquid phase appears during the decomposition. The point at which this happens, and the rate of decomposition in the early stages, depend on the conservation within the system of slightly volatile products such as benzoic acid and diphenyl which, initially, may be lost by vapour phase diffusion at a rate comparable with their rate of formation. Results are correlated, over the whole course of the decomposition, by a combination of conventional rate equations and an approximation to the phase equilibrium between undecomposed peroxide and condensed products.

October, 1964

JFRD report: Fire research note.

Benzoyl peroxide: (decomposition: thermal)

Results: benzoyl: decomposition: thermal

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INTRODUCTION

Studies of the thermal explosion of higher molecular weight organic peroxides of industrial importance, to be reported elsewhere, have indicated the need for information on the kinetics of the decomposition of these compounds in the pure, or nearly pure, state. Apart from some observations by Farmer⁽¹⁾ on the early stages of the decomposition of benzoyl peroxide in vacuo, published kinetic studies on these compounds are largely confined to their decomposition in solvents and their role as polymerisation initiators.

This paper describes the isothermal decomposition of benzoyl peroxide, at atmospheric pressure, at temperatures below its melting point. The decomposition of this peroxide is accompanied by progressive liquefaction. The rate of decomposition has been found, irrespective of any self-heating, to depend on the dimensions of the sample, and it can be profoundly affected by artificial adjustment of the partial vapour pressures of certain of the known⁽²⁾ condensed decomposition products, such as benzoic acid, diphenyl and phenyl benzoate, in the system. In view of the physical complexity of the decomposition the approach has been, first, to study the whole course of the decomposition at different temperatures but with other conditions constant; this has provided a basis for the choice of rate equations. Then other conditions have been varied to obtain limiting values of the rate constants believed to be appropriate to decomposition of the peroxide in bulk - this being a principal object of the investigation. Because also, it was desired to obtain an insight into the behaviour of benzoyl peroxide as used industrially, the peroxide has been studied initially in the form marketed without further purification.

The effect of certain possible impurities becomes obvious in the present study, but this aspect is being investigated further and will be discussed elsewhere.

EXPERIMENTAL

Procedure

Weighed specimens of the peroxide, of about 0.2 g, in tubes of borosilicate glass lightly capped with aluminium foil, were heated in oil baths maintained to within $\pm 0.2^\circ\text{C}$ of a series of fixed temperatures between 70 and 95°C. Tubes were withdrawn at intervals and the residual peroxide determined by the iodometric method of Wagner, Smith and Peters⁽³⁾ using isopropyl alcohol as solvent. The following variants were studied:-

1. Relatively shallow layers of large diameter; i.e. 0.2 g in test tubes 14 mm diameter and 125 mm in length, the depth being about 5 mm at the centre.
2. Deeper layers of small diameter; i.e. 0.1, 0.2, or 0.4 g in tubes 4 mm diameter x 150 mm in length, the corresponding depths being 12, 24 and 48 mm respectively.
3. 0.2 g in the tubes of 14 mm diameter with a bead of benzoic acid fused on to the wall 1 - 2 cm above the peroxide in order to maintain a nearly saturated vapour pressure of benzoic acid over the peroxide. A few

experiments of this type were also carried out in which molten diphenyl or phenyl benzoate was suspended above the peroxide, either as a hanging drop or absorbed in a cigarette filter.

Two different batches of benzoyl peroxide were used. Batch A, which was of 98.4 per cent purity as determined by the above analytical method, was stored moistened with water and either used moist (Sample A1, moisture content approximately 25 per cent) or dried in a vacuum oven for 3 hours at 40°C as required for use (Samples A2, A3 and A4). Batch B of 98.2 per cent purity, was kept and used dry.

Minor ancillary experiments are described briefly later as required.

RESULTS

The course of the decomposition of the peroxide at different temperatures is shown in Figs 1-3. In order to avoid confusion between different sets of results those for the 0.2 g samples in wide tubes, for which decomposition was followed to completion, are given as the fractional loss of peroxide, and most of the rest as the fractional residue of peroxide. Detailed analysis of the results is reserved for a later section; here certain qualitative features are pointed out.

The results lie on curves of the sigmoid form commonly observed for the decomposition of solids and there is an induction period which, broadly speaking, increases by a factor of ten for a decrease in temperature of 10°C. As is to be expected, since each observation corresponds to a different specimen of peroxide, there is considerable scatter in the results. It appears from the results at 80°C that there can be a real though minor difference between different dried samples (A2, A3) of a given batch.

At the degree of decomposition corresponding to points S in Figs 1-3 the peroxide particles became noticeably sticky; this was taken to indicate the first appearance of the liquid phase. At the degree of decomposition corresponding to points L, the residue became completely liquid. Between S and L solid and liquid phases were present together. In the 4-mm tubes, liquid usually drained away from the solid as it appeared and this was associated with a reduction in the rate of decomposition in the later stages; for this reason the decomposition could not always usefully be followed to completion in the narrow tubes.

As decomposition proceeded the residue became yellow, the yellow colour appearing before melting was noticeable (this coloration did not, however, interfere with the end-point of the iodine titration until decomposition was about 95 per cent complete). The residue after complete decomposition was mainly resinous when cooled to room temperature; it melted, i.e. became obviously fluid, between 50 and 60°C.

Laminar crystals collected in the cool regions at the tops of the tubes during decomposition. These crystals had a melting point of 120°C and were accordingly presumed to be benzoic acid⁽²⁾. Part of the sublimate was apparently present initially as impurity in the peroxide. For example, at 80°C a trace appeared within the first 10 minutes but, when this was removed, a further deposit appeared much more slowly. The initial deposit was not identified.

Considering next the effect of varying the depth of the specimen it will be seen that, at 70°C, results for depths of 24 and 48-mm in tubes of 4-mm diameter lie on a curve with an inflexion at about 470 hours instead of the 950 hours for 5-mm layers in the wider tubes. The appearance of liquid phase was detectable at about half the degree of decomposition at which it was first seen in the shallow samples. These effects are independent of batch (compare

A1 and B in 14-mm tubes). There is no difference apparent between the results for depths of 24 and 48-mm and it is concluded that the effect of increasing the depth at this temperature has reached a maximum.

At 90°C (Fig. 3) on the other hand, results for samples having a depth of 24 mm in 4-mm tubes lie on or near the curve for the shallow layers.

At 80°C, results for decomposition of 5-mm layers in the presence of a bead of benzoic acid lie on a curve with an inflexion at 48 hours, compared with the 74 hours when benzoic acid was absent. At this temperature, results for 12 mm and 24-mm layers in 4-mm tubes also lie on this curve, except towards the end of the decomposition when drainage of liquid phase began to occur. Again liquid phase appears at a lower degree of decomposition than in the shallow layers. Thus the maintenance of a high vapour pressure of benzoic acid has the same effect as increasing the depth of layer at 80°C.

The presence of benzoic acid makes no difference to the course of the decomposition at 70°C. When however a high vapour pressure of diphenyl was maintained above a 5-mm layer of peroxide, decomposition was rapid; 77.5 per cent decomposition occurred in 70 hours compared with 950 hours for the peroxide on its own. In the presence of phenyl benzoate 8.3 per cent of the peroxide decomposed in 70 hours.

These effects suggest that certain of the condensed products, such as the three mentioned above, play an essential role in the decomposition but, in the early stages, the rate of formation of these products may be little more than their rate of loss from the system by vapour phase diffusion. Hence, any factor tending to favour the accumulation of these products in the system, such as increasing their partial vapour pressures externally or increasing the depth of layer, should hasten the decomposition. An artificial increase in the partial pressure of a particular product can also, of course, lead to a transfer of that product from the vapour to the condensed phase and so make the decomposition abnormally fast.

Although certain of the products can take a further part in the reaction, it seems that their action depends at least partly on their ability to form low melting mixtures with the peroxide; i.e. they are responsible for the early appearance of liquid phase with which acceleration of the decomposition of solids is commonly associated. Thus, mixed melting-point determinations showed that benzoic acid forms an approximately equimolecular eutectic with benzoyl peroxide which melts at about 85°C; diphenyl forms an eutectic with the peroxide, in the proportions of about 4 moles of the former to one of the latter, which melts at 55°C. Although, in practice, the system is not a simple binary mixture these results suggest that benzoic acid will contribute to the formation of the liquid phase at temperatures near 80°C but not at 70°C; whereas at 70°C the conservation of diphenyl can lead to the early formation of the liquid phase.

Participation in the formation of the liquid phase cannot, however, be the only function of these products. At the lower temperatures, the decomposition is advanced before liquid appears, e.g. 27 per cent for the shallow layers at 70°C; hence these products must also affect the rate of the purely solid phase decomposition.

The rate of loss of pure diphenyl from one of the 14 mm diameter tubes at 80°C was found to be 5 times greater than the loss of pure benzoic acid; the actual rates were $1 \times 10^{-7} \text{ g s}^{-1}$ for the former and $2 \times 10^{-8} \text{ g s}^{-1}$ for the latter and were about 4 times greater than estimated for loss by simple diffusion without convection. Thus, diphenyl is less likely to be involved in the early stages, and at the higher temperatures, than is the less volatile benzoic acid.

Finally, anticipating an Arrhenius-type dependance of decomposition rate on temperature, it may be expected that the importance of the above effects will diminish at the higher temperatures when the rate of formation of products in the early stages of the decomposition becomes much greater than their loss by diffusion.

SELF-HEATING

Four out of five specimens heated at 95°C exploded after 40 ± 0.5 min. It will be assumed that the explosion was purely thermal in origin and, before proceeding with an analysis of the results, an assessment will be made of the magnitude of self-heating at the lower temperatures.

The behaviour of the peroxide at 95°C indicates that the critical size for thermal explosion at this temperature is close to that of the 0.2 g samples in 14 mm tubes. This implies further that the maximum sub-critical temperature increase at the centre of the specimen will occur at a bath temperature close to 95°C. It will be assumed for the moment that the specimens in the 14-mm tubes were spherical. Thermal ignition theory, for conductive heat transfer in the specimen, then gives the maximum sub-critical temperature increase as $1.6 RT_A^2/E$ (4) where E is the activation energy and T_A the bath temperature. For $E = 41,000$ cal/mole (see later section) and $T_A = 368^\circ\text{K}$, this increase is 11 deg C. (The activation energy appropriate to thermal explosion will be discussed in a later paper: here the lowest observed value is used and this has the effect of overestimating the sub-critical temperature rise).

At bath temperatures below the critical we have:-

$$\delta/\delta_c = \left(\frac{T_{Acrit}}{T_A}\right)^2 \exp \frac{E}{R} \left(\frac{1}{T_{Acrit}} - \frac{1}{T_A}\right)$$

Where δ and δ_c are respectively sub-critical and critical values of Frank-Kamenetskii's self-heating parameter (4) corresponding to the sub-critical and critical bath temperatures T_A and T_{Acrit} .

At a bath temperature of 90°C, and with E as above $\delta/\delta_c = 0.46$. Corresponding to this ratio we have $\theta_o/\theta_{ocrit} = 0.2$ (5) where θ_o and θ_{ocrit} are sub-critical and critical dimensionless temperature increases at the centre of the specimen defined in the usual way as $\theta_o = \frac{E}{RT_A^2} \Delta T$,

ΔT being the temperature increase in deg C. Hence

$$\Delta T = 0.2 \left(\frac{T_A}{T_{Acrit}}\right)^2 \Delta T_{crit} = 2 \text{ deg C}$$

Measurement with a differential thermocouple of 34 S.W.G. platinum/platinum rhodium indicated a maximum temperature rise of 1.5-2°C at 90°C.

Proceeding in the same way, the possible temperature increase in the specimen at a bath temperature of 80°C is calculated as 0.3 deg C.

The actual geometrical form of the specimens in the 14-mm tubes lay between that of a sphere and a hemisphere, of which the latter, having a larger surface to volume ratio, can accommodate a higher maximum sub-critical temperature increase. The possible temperature increases have therefore been slightly underestimated.

The specimens in 4-mm tubes approximated to infinite cylinders having a radius of the same order as that of the sphere assumed for the specimens in 14-mm test tubes; the temperature increases will have been correspondingly less (4).

It is concluded that, at 90°C the rate of decomposition is likely to have been increased slightly by self-heating when the rate was near its maximum; but at the lower bath temperature used, and in all cases during the early stages of the decomposition, the effect was negligible.

ANALYSIS OF RESULTS

General

Hinshelwood⁽⁶⁾ first showed that the acceleration of the decomposition of an organic solid (tetryl) could be accounted for quantitatively by the appearance of a liquid phase, but his study was restricted to a small range of decomposition only. Rate equations designed to cover the whole range of decomposition, when the decomposition in both phases is first order, have been proposed by Bawn⁽⁷⁾ and elaborated by Manelis and Dubovitskii⁽⁸⁾ but do not hitherto appear to have received any application. The following analysis of the decomposition of benzoyl peroxide employs a modification of Bawn's model.

The basic assumption common to these earlier treatments is adopted; this is that, so long as the rate of decomposition is low, the system will not be far removed from solubility equilibrium. In so far as this assumption is valid, and neglecting the actual complexity of the system indicated earlier, the points of first appearance of the liquid phase and of complete liquefaction in Figs 1-3 may be used to sketch a "binary" phase equilibrium diagram for benzoyl peroxide and undifferentiated condensed decomposition products. This is shown in Fig. 4, the S and L points from Figs 1-3 (shallow specimens in 14 mm tubes) lying on the solidus and liquidus curves respectively. The diagram has been completed tentatively below 70°C assuming, for simplicity, the existence of a continuous series of solid solutions between the peroxide and its decomposition products down to about 50°C.

The "solid solution" may exist as a separate solid phase on the surface of undecomposed peroxide. The solidus curve in Fig. 4 will not then represent the composition of the solid solution alone, but no allowance can be made here for this possibility.

An equilibrium diagram of the form shown in Fig. 4 implies that the decomposition of the peroxide can take place in three stages at temperatures below its melting point. Initially there will be solid phase decomposition with condensed products remaining in solid solution with undecomposed peroxide. This will be followed by decomposition in solid and liquid phases of fixed composition (with respect to undecomposed peroxide) and varying proportions and, finally, the solid phase will disappear and decomposition of the residual peroxide will continue in the liquid phase. In these respects, the course of the decomposition has similarities with the decomposition of potassium perchlorate⁽⁹⁾.

The loss in weight of benzoyl peroxide was found to be only about 18 per cent when decomposition was complete. Rate equations based on the above model will, therefore, not be corrected for the change in volume of the system as attempted by Manelis and Dubovitskii⁽⁸⁾.

Rate equations

The final liquid phase decomposition can be fitted to the first order law:

$$-\frac{d(1-x)}{dt} = \frac{dx}{dt} = k_1(1-x) \quad ; \quad x_1 \leq x \leq 1 \quad (1)$$

where x is the fraction of peroxide decomposed at time t , k_1 the rate constant and x_1 the degree of decomposition at which the solid phase disappears. This is shown in Figs 5 and 6, where $\log(1-x)$ is plotted against time for the results at 90°C (Sample A2) and 70°C (Sample A1); these two examples have been chosen to illustrate the extremes obtained in the degree of fit to a straight line.

The choice of rate equation for the initial solid phase decomposition is somewhat arbitrary since the extent of decomposition covered is generally too

small, and the scatter of the results too great, to permit a convincing test of any given equation. However, the rate of decomposition in this stage increases with time and the simplest form of equation for an autocatalytic process will be used, viz:

$$\frac{dx}{dt} = k_s x(1-x) \quad (2)$$

with the usual initial condition $x = x_0$ at $t = 0$, so that $x_0 \leq x \leq x_s$ where x_s is the degree of decomposition at which the liquid phase first appears. Equation (2) is of course, when integrated, formally equivalent to the Prout-Tompkins equation which is based on a branching process and was originally proposed to account for the decomposition of certain inorganic solids; Vaughan and Phillips⁽¹⁰⁾ have shown it to be applicable to the decomposition of an organic compound - a nitrobenzenediazo-oxide - which decomposed without melting.

Results for the solid phase decomposition are plotted in Figs 5 and 6 as $\log \frac{x}{1-x}$ vs t . Usually the points were scattered as in Fig. 6, and straight lines fitted by the method of least squares were used to estimate x_0 and k_s .

In the intermediate stage of the decomposition when two phases are present, the fraction of undecomposed peroxide in the solid and liquid phases remains constant at $1 - x_s$ and $1 - x_l$ respectively if the assumption of quasi-equilibrium is fulfilled. The total rate of disappearance of peroxide from the system is then given by

$$-\frac{d(1-x)}{dt} = \frac{dx}{dt} = r_s \frac{x_l - x}{x_l - x_s} + r_l \frac{x - x_s}{x_l - x_s} \quad (3)$$

for $x_s \leq x \leq x_l$

where

$$r_s = k_s x_s (1 - x_s) \quad = \text{rate in solid phase}$$

and

$$r_l = k_l (1 - x_l) \quad = \text{rate in liquid phase.}$$

Equation (3) may be rearranged to

$$\frac{dx}{dt} = K(x + a) \quad (4)$$

where

$$K = \frac{r_l - r_s}{x_l - x_s} \quad \text{and} \quad a = \frac{r_s x_l - r_l x_s}{r_l - r_s} \quad (5)$$

Equation (4) is of the same form as that obtained for the simpler model of first order decomposition in both phases considered by Bawn⁽⁷⁾ and Manelis and Dubovitskii⁽⁸⁾; Bawn's equation can be derived as a special case of this slightly more general model.

Integration of equation (4) with the condition $x = x_s$, $t = t_s$, gives

$$\ln \left(\frac{x+a}{x_s+a} \right) = K(t - t_s) \quad (6)$$

It may be noted that, when $x = x_l$, the argument of the left-hand-side of equation (6) is equal to the ratio of the rates of decomposition in the liquid and solid phases when both are present.

Experimental results for the intermediate stage of decomposition are plotted for the two examples in Figs 5 and 6, as $\log(x + \frac{a}{k_1})$ vs. t with $\frac{a}{k_1}$ calculated from the appropriate values of x_s and x_l , and with k_s and k_l obtained from the stages of solid and liquid phase decomposition respectively. At 70°C (Fig 6) the relationship is linear as required by equation (6); at 90°C there is a departure from linearity evident in the higher values of $(x + \frac{a}{k_1})$ which can be attributed to self-heating in the specimen.

Rate constants

The rate constants for the solid and liquid phase decomposition in the shallow layers of peroxide in the 14-mm diameter tubes, calculated by the method of least squares from the above linear representations of the results, are plotted logarithmically in Fig. 7 against the reciprocals of the absolute temperatures. The value of k_l for some results at 85°C (not shown) is included, but the scatter of the results in the early stages of the decomposition at this temperature was too great for a useful k_s to be obtained. The results for samples A2 and A3 were combined for the calculation of k_s at 80°C. Values of x_0 associated with each value of k_s are given in brackets in the figure.

It will be seen from Fig. 7 that x_0 is small and independent of temperature. The high value of 0.005 at 70°C obtained for the moist peroxide sample (A1), in 14mm tubes is not regarded as significant as it may easily be due to a small error in the estimated moisture content.

The rate constants for decomposition in specimens of increased depth, or with the vapour pressure of benzoic acid artificially increased over shallow layers, are also plotted in Fig. 7. As indicated earlier, these are likely to be limiting values applicable to much greater depths, i.e. to the peroxide in bulk. All results here are for batch B peroxide.

It will be seen that one effect of increasing the depth of layer, or the vapour pressure of benzoic acid, is to increase the value of x_0 . This is not due to a difference in batch (compare sample B at 70°C in wide tubes, for which $x_0 = 0.002$, Fig. 7) but may be associated with a reduced loss of the trace substance observed to sublime within the first ten minutes or so from the shallower layers at 80°C. Values for k_l derived entirely from results for shallow layers in the presence of benzoic acid vapour, at 80°C and 85°C lie about the line obtained for k_l determined in the absence of benzoic acid (Fig. 7). As far as could be determined, liquefaction occurred at about the same degree of decomposition as for shallow layers in the absence of benzoic acid.

Arrhenius constants

The graphs of the rate constants in Fig. 7 are reasonably linear and the Arrhenius equations are found to be

$$k_l = 10^{20.4} e^{-\frac{40500}{RT}}, \quad k_s = 10^{38.4} e^{-\frac{69800}{RT}}$$

for decomposition in the shallow layers, and

$$k_s = 10^{30.3} e^{-\frac{56500}{RT}}$$

for deep layers.

The apparent activation energy and frequency factor for the liquid phase decomposition are high but within the range reported for the thermal decomposition of other condensed organic compounds - mainly explosives (7) (11). They are higher than for the decomposition of benzoyl peroxide in common solvents, for which the activation energy has a value close to the dissociation energy of the peroxide bond. However, it may be noted that the value of k_l at 80°C is within the range reported (2) for this constant for decomposition of the peroxide in solvents.

The activation energies for the solid phase decomposition are also high, again as commonly observed for solids, but the "frequency factor" for the decomposition of the solid in the shallow layers is exceptionally high. Both the activation energy and frequency factor decrease when the depth of layer is increased.

Clearly the simple rate equations that have been fitted to the solid and liquid phase decompositions cannot imply a corresponding simplicity in mechanism and, in the solid phase decomposition, control of the decomposition by physical factors may also be suspected.

DISCUSSION

The main test of the model used in this analysis of the results lies in the fit of the equation for the intermediate stage of the decomposition for which both phases are present together and which, in the temperature range studied, covers 40-60 per cent of the decomposition. It will be noted that the form of the rate equation for this stage depends only on the assumption of phase equilibrium and not on the form of the rate equations chosen for the separate phases.

The plot of $\log(x + a)$ against time gave a satisfactory straight line in all cases, but this is not a particularly severe test. In Table 1, "observed" values of K obtained from the slopes of these lines are compared with corresponding values of K calculated from equation (5) with the aid of k_1 , k_s , x_1 and x_s taken from Figs. 4 and 7; values in the table refer to layers 5 mm deep - some in the presence of benzoic acid.

Table 1

Decomposition of benzoyl peroxide

$$x_s \leq x \leq x_1$$

Sample	Temperature °C	K_{obs} s^{-1}	$\frac{K_{obs}}{K_{calc}}$	$\frac{\text{Rate in liquid}}{\text{Rate in solid}}$
A1	70	1.9×10^{-6}	1.4	3.3
A2	80	2.3×10^{-5}	1.5	4.0
A2	90	1.8×10^{-4}	1.2	5.8
B*	80	1.5×10^{-5}	1.2	5.9
B*	85	5.3×10^{-5}	1.2	7.0

* In presence of benzoic acid

The observed values of K are consistently higher than the calculated values. Thus, the rate of decomposition in the intermediate stage becomes progressively greater than predicted by the weighted sum of the rates in the solid and liquid phases (equation (3)). Under conditions favouring the conservation of products, the discrepancy in K is 20 per cent.

The most uncertain quantity in the calculation of K is x_s which rests on visual observation of the appearance of liquid phase and which, in any case, may represent a mean composition for a multicomponent solid surface phase and pure bulk solid. However, K is not very sensitive to changes in x_s and the most probable reason for the discrepancy is simply that the binary model adopted is an oversimplification of the actual system. A possible effect capable of accounting for the higher rates of decomposition observed is that, as decomposition proceeds in the liquid phase this phase may become a progressively better solvent for the solid - so that the liquidus curve in Fig. 4 represents the final composition of the liquid phase with respect to

peroxide in the intermediate stage; this would lead to a progressive increase in in equation (3).

Nevertheless, the agreement obtained suggests that the course of the decomposition is in fact dominated by the accumulation of the liquid phase in which undecomposed peroxide dissolves, and the simple binary model is adequate for the purposes of this work. For application to the question of the occurrence of thermal explosion (to be discussed elsewhere) the maximum rate of decomposition in the temperature range in which two phases can exist may be taken as

$$\left(\frac{dx}{dt}\right)_{\max} = k_{obs} (x_1 + x_2)$$

Also included in Table 1 are the ratios of the rates of decomposition in the liquid and solid phases when both phases are present together. Calculated for the model used in this paper, these ratios are not large (compare Bawn (7)).

Finally, if it is supposed that benzoic acid comprises about 25 per cent of the condensed decomposition products (12) it can be estimated that its rate of formation will be equal to its rate of loss by diffusion when the extent of decomposition is about 1 per cent. This confirms the reasonableness of arguments invoking the near equality of these rates in the early stages of the decomposition in shallow layers.

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REFERENCES

- (1) FARMER, R. C. The stability of benzoyl peroxide. J. Soc. Chem. Ind., 1921, 40 84T.
- (2) TOBOLSKY, A. V. and MESROBIAN, R. B. Organic peroxides. Interscience Publishers Inc. New York, 1954.
- (3) WAGNER, C. D., SMITH, R. H. and PETERS, E. D. Determination of organic peroxides. Ind. Eng. Chem. (Anal.), 1947, 19 976.
- (4) FRANK-KAMENETSKII, D. A. Diffusion and heat exchange in chemical kinetics. Translated by THON. Princeton University Press. Princeton, 1955.
- (5) THOMAS, P. H. and BOWES, P. C. Some aspects of self-heating and ignition in cellulosic materials. Brit. J. Appl. Phys., 1961, 12, 222, Fig. 6 and Appendix I.
- (6) HINSHELWOOD, C. N. Some physico-chemical problems connected with the stability of explosives. J. Chem. Soc., 1921, 119 721.
- (7) BAWN, C. E. H. The chemistry of the solid state. Editor GARNER, W. E. Butterworths Scientific Publications. London, 1955. p. 254.
- (8) MANELIS, G. B. and DUBOVISKII, F. I. Thermal decomposition of explosives below the melting point. Doklady. Akad. Nauk. SSR. 1959, 126, 813.
- (9) HARVEY, A. E. et al. The kinetics of the thermal decomposition of potassium perchlorate. J. Amer. chem. Soc., 1954, 76, 3270-3.

- (10) VAUGHAN, J. and PHILLIPS, L. Thermal decomposition of explosives in the solid phase. J. Chem. Soc., 1947, 1560.
- (11) COOK, M. A. The science of high explosives. Reinhold Publishing Corporation. New York, 1958.
- (12) ERLÉNMEYER, H. and SCHOENAUER, W. The thermal decomposition of di-acyl peroxides. Helv. chim. acta. 1936, 19 338.

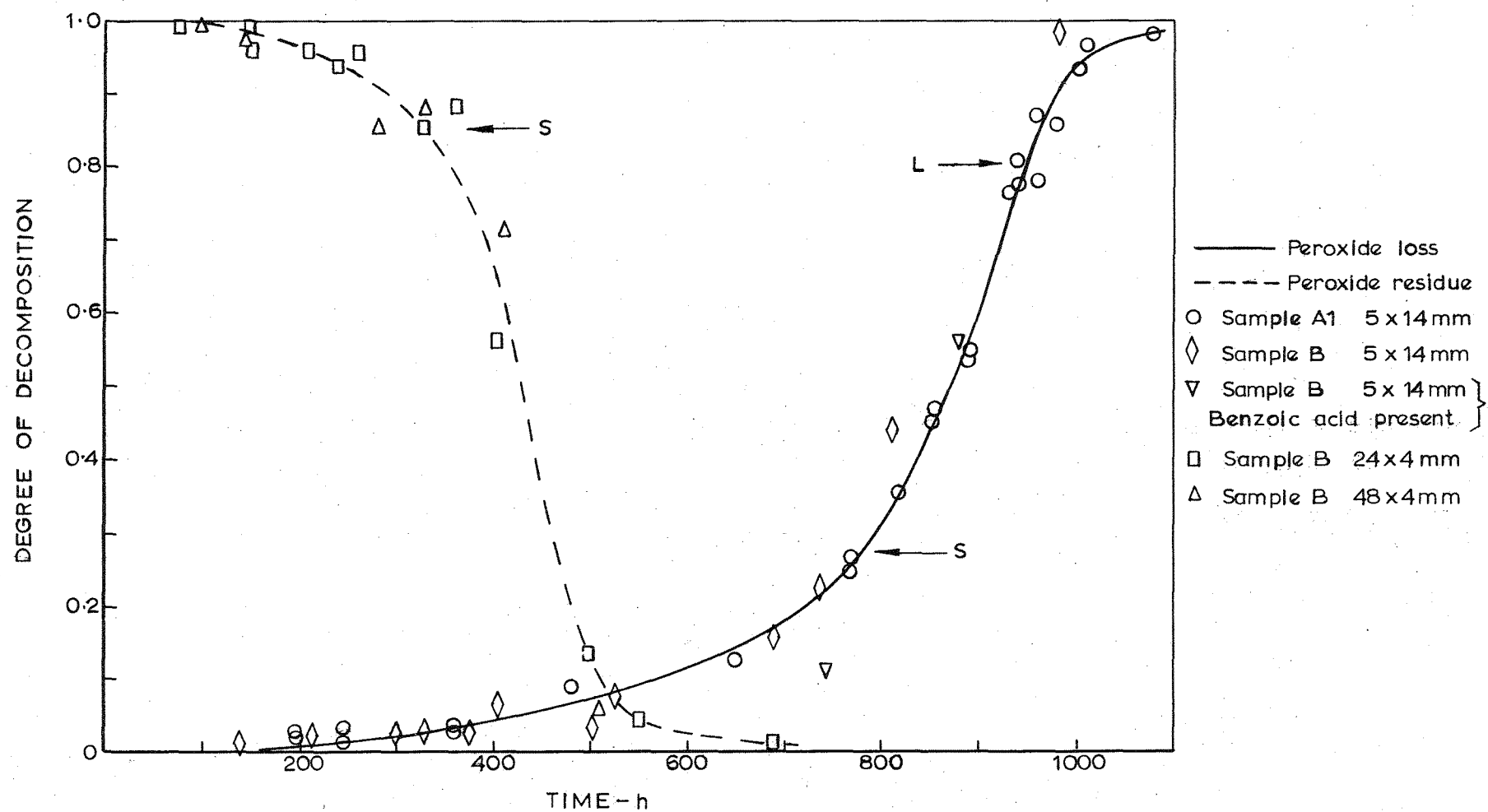


FIG.1. DECOMPOSITION OF BENZOYL PEROXIDE AT 70 °C

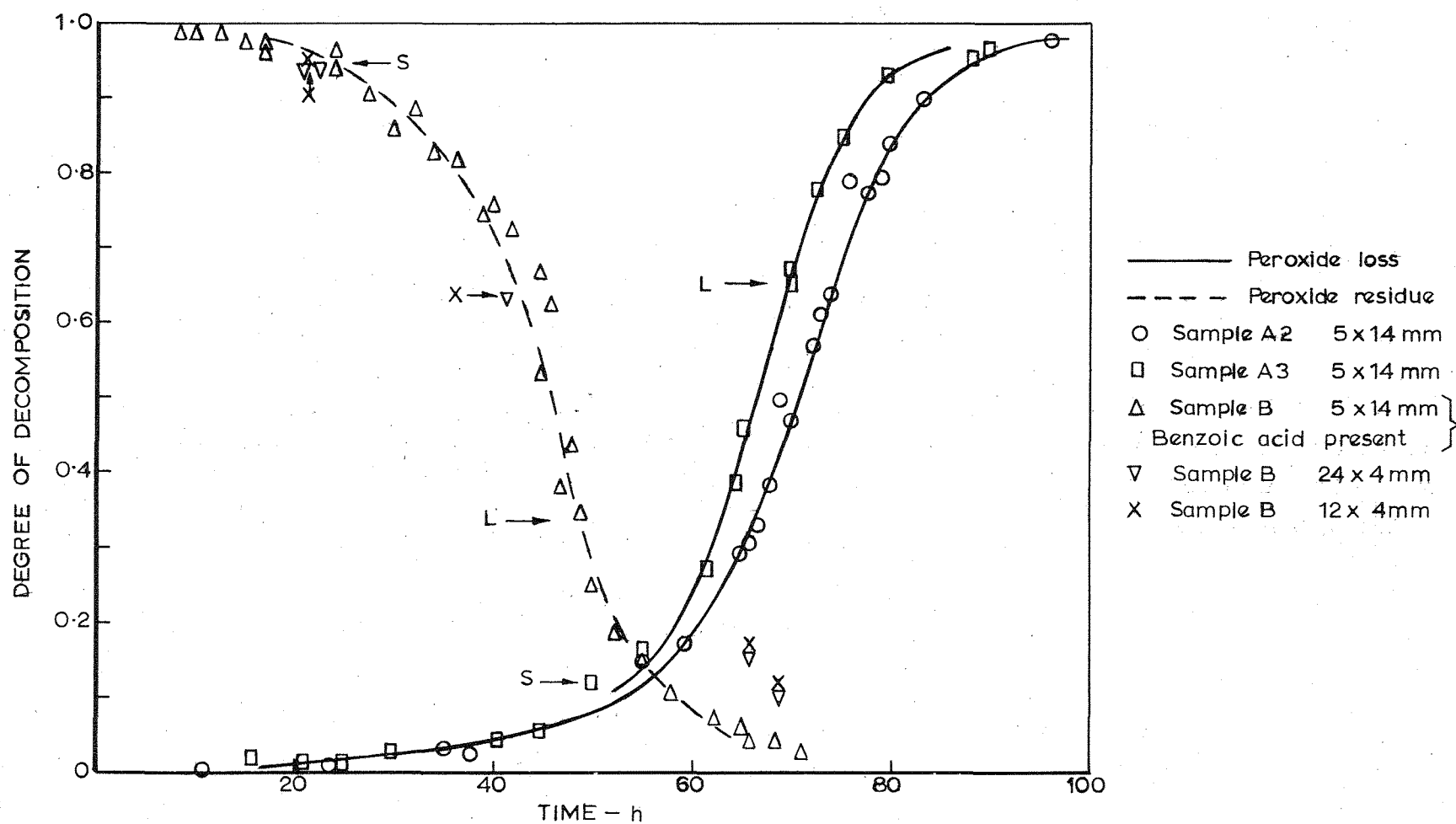


FIG.2. DECOMPOSITION OF BENZOYL PEROXIDE AT 80°C

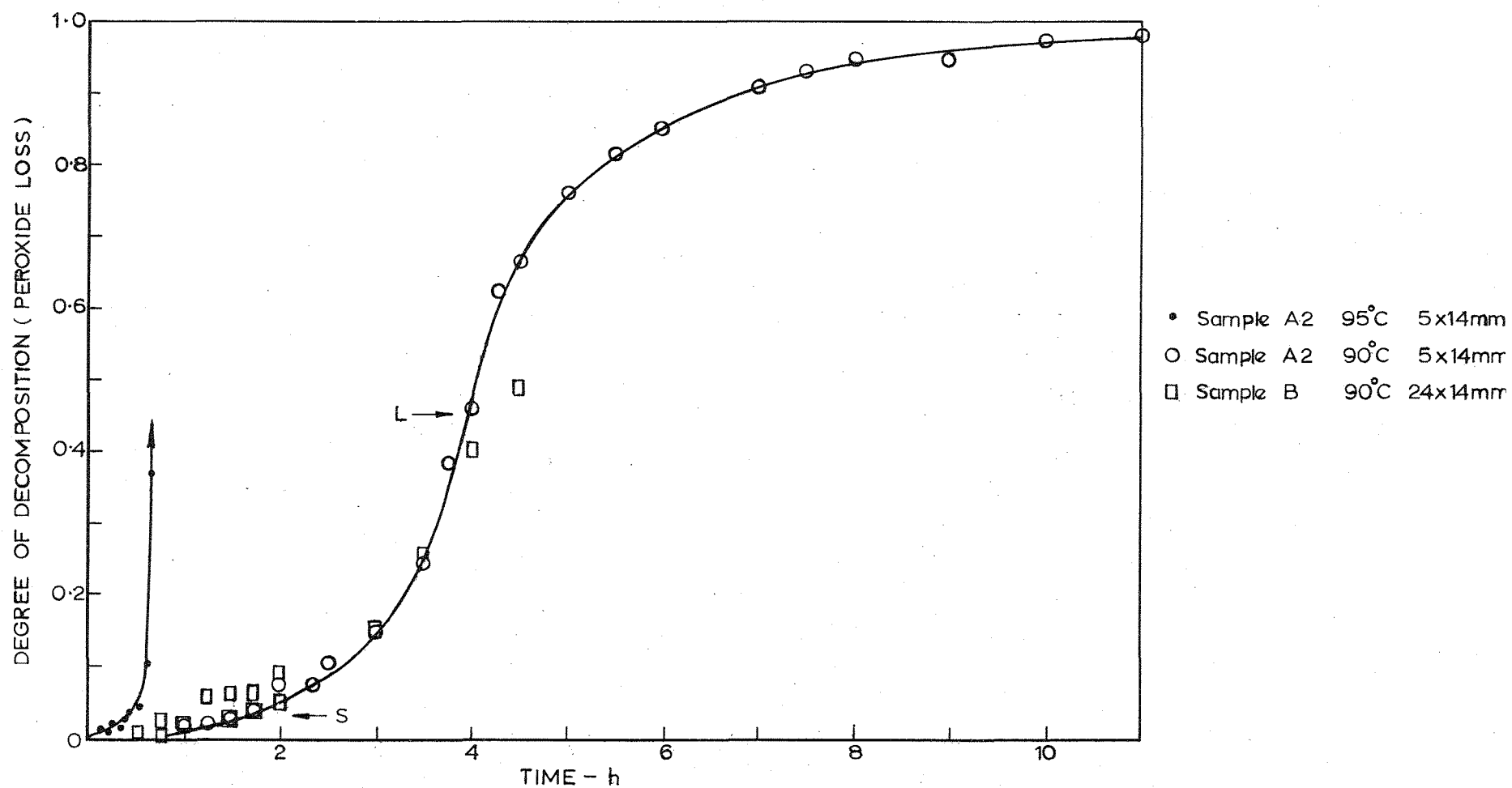


FIG.3. DECOMPOSITION OF BENZOYL PEROXIDE AT 90 AND 95°C

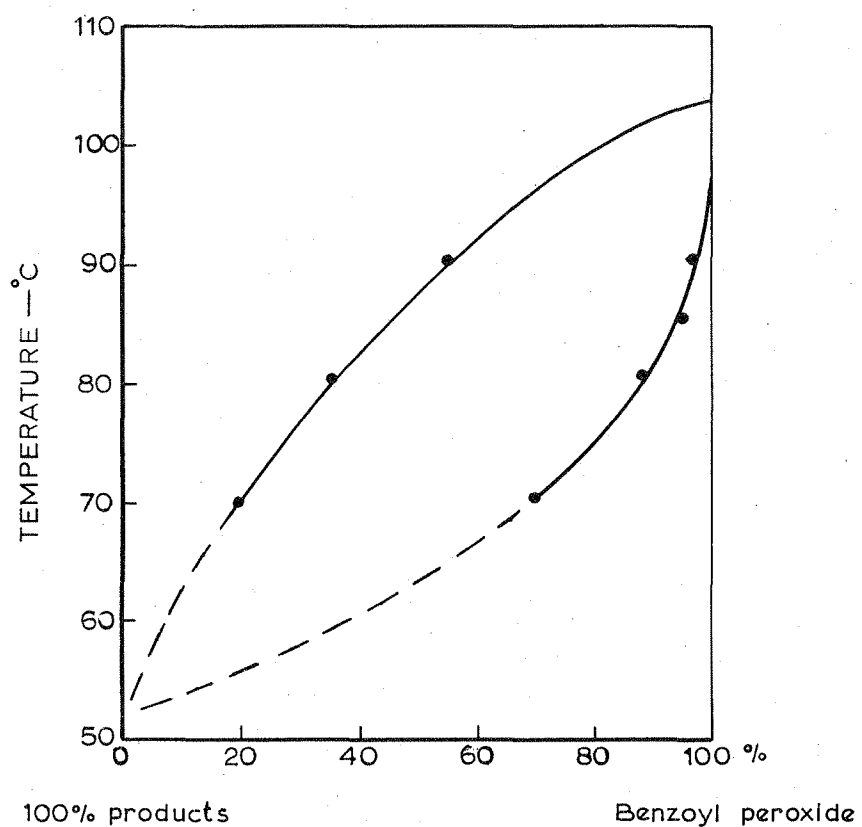


FIG.4. "EQUILIBRIUM" DIAGRAM FOR BENZOYL PEROXIDE AND CONDENSED DECOMPOSITION PRODUCTS

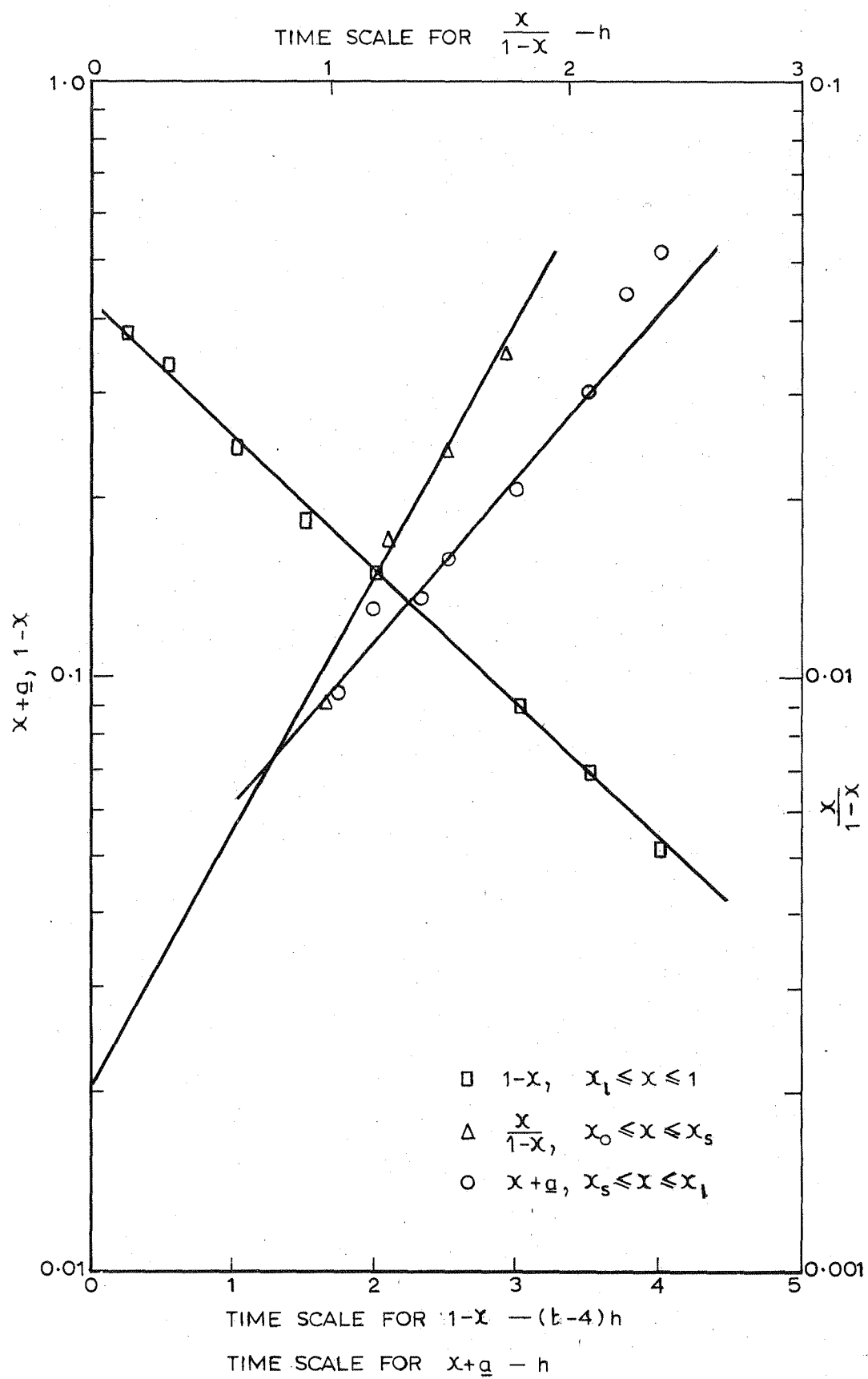


FIG.5. ANALYSIS OF RESULTS FOR DECOMPOSITION
AT 90°C (SAMPLE A2)

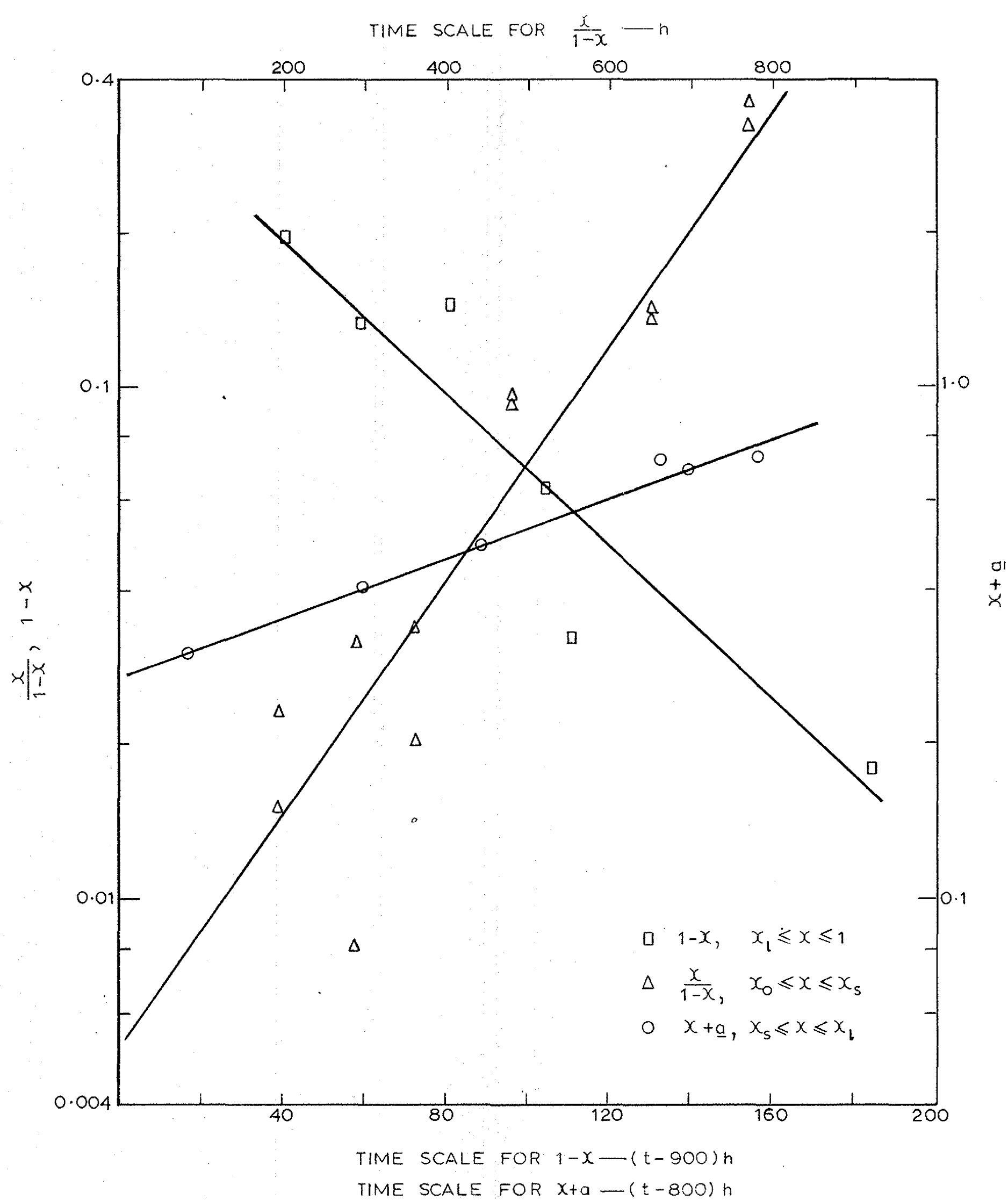


FIG.6. ANALYSIS OF RESULTS FOR DECOMPOSITION AT 70°C (SAMPLE A1)

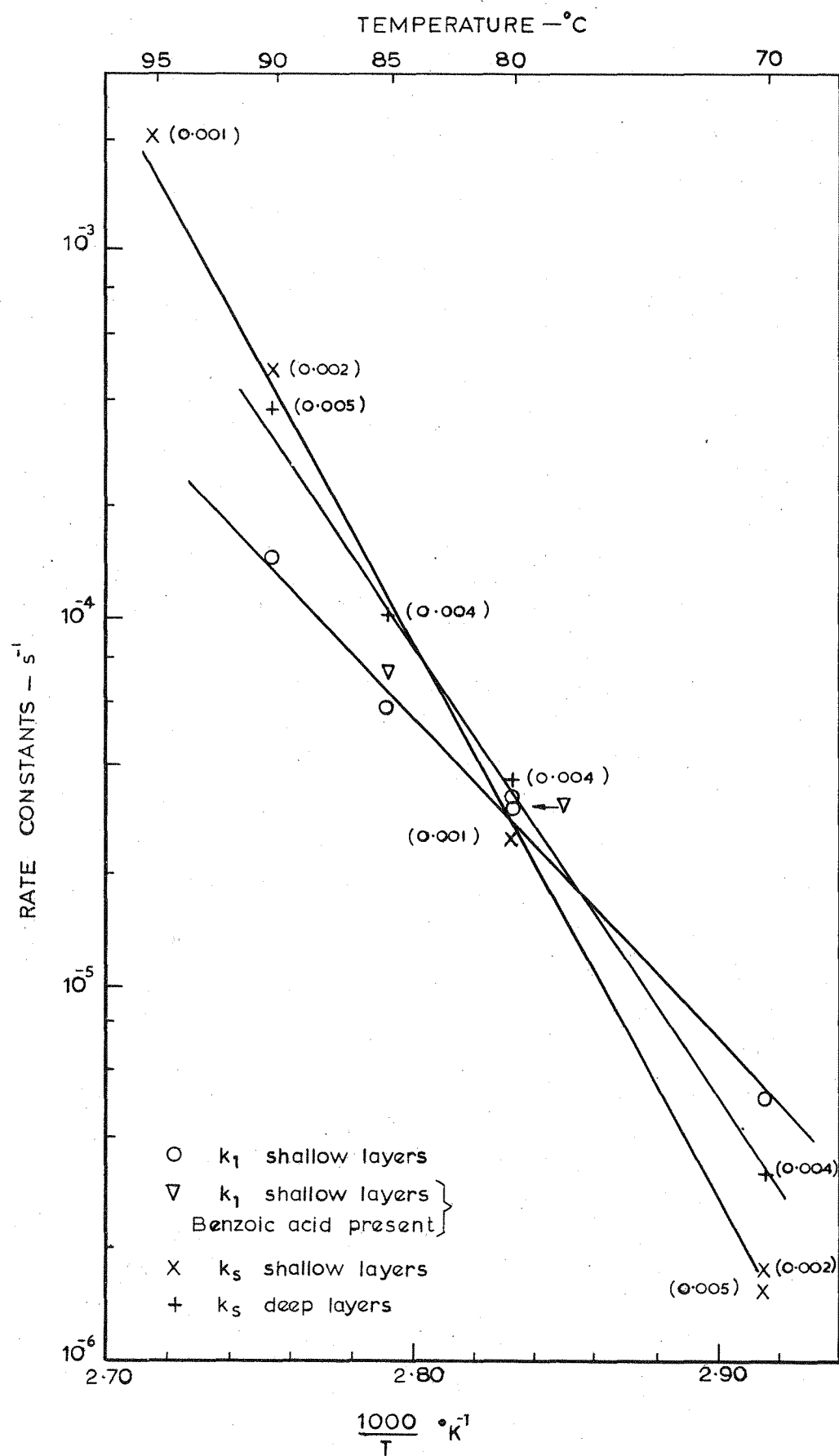


FIG.7. RATE CONSTANTS