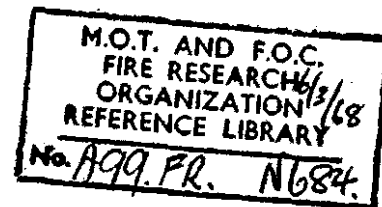# Fire Research Note
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THERMAL DECOMPOSITION OF LAUROYL PEROXIDE

by

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FIRE
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SUMMARY

The isothermal decomposition of lauroyl peroxide has been studied and compared with that of benzoyl peroxide.

The results, together with an estimate of the heat of decomposition, are used to discuss the likelihood of thermal explosion in the transport and storage of lauroyl peroxide. It is concluded that the safety of the peroxide, in this respect, depends heavily on the existence of a long induction period for explosion which decreases very rapidly as the ambient temperature is increased.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE

JOINT FIRE RESEARCH ORGANIZATION

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P.C. Bowes and June Harris

INTRODUCTION

This note reports an investigation of the isothermal decomposition of lauroyl peroxide at different temperatures and forms part of a study of the thermal decomposition and explosion of unstable compounds. The work is complementary to similar studies of benzoyl peroxide[1, 2]; lauroyl peroxide being chosen as a commonly used organic peroxide which, compared with unphlegmatised benzoyl peroxide, is insensitive to initiation by impact and friction and is regarded as relatively safe to handle.

The decomposition has been followed at temperatures both below and above the melting point of the peroxide, usually to near completion. Since it was desired to determine the behaviour of the peroxide as used in practice, the commercially available peroxide was used without purification.

The main objective has been to obtain rate constants which may be used in a thermal explosion model, but a number of additional features of the decomposition are noted briefly for the sake of their interest in the general field of the thermal decomposition of organic peroxides. •

EXPERIMENTAL

Material

The lauroyl peroxide used was of 97 per cent purity (determined by peroxide assay) and had a melting point of 54°C. It is understood that the commercially available lauroyl peroxide may contain small quantities of the diacyl peroxides of fatty acids adjacent to lauric acid but is otherwise a single substance.

Thermal decomposition

As in previous studies of benzoyl peroxide[1], the decomposition of the lauroyl peroxide was followed by determining the residual peroxide in small samples maintained for different periods at a given temperature.

The peroxide samples, of about 0.2 g, were heated in tubes of borosilicate glass 14 mm diameter and 125 mm length lightly capped with aluminium foil; the maximum depth of sample in these tubes was about 5 mm.

As a check on the possible loss of volatile decomposition products important to the decomposition process[1], some comparative tests were carried out with 0.2 g of peroxide in tubes 4 mm diameter in which the sample depth was 24 mm.

The residual peroxide was determined by the iodometric method of Wagner, Smith and Peters[3] modified to the extent that the quantity of isopropyl alcohol solvent was halved and the sodium iodide was added as a solid.

Temperatures were usually controlled to within $\pm$ 0.2 deg C, but, on some occasions (which will be indicated) the temperature controller operated less satisfactorily and the variation was greater.

<div align="center">DISCUSSION OF RESULTS</div>

Qualitative features

The range of behaviour observed for the isothermal decomposition of the lauroyl peroxide is shown in Figs 1-3 where the fraction of peroxide decomposed, denoted by x, is plotted as a function of time; Fig 1 includes the results for decomposition in 4 mm tubes. The relatively large scatter in the results at 50.5°C is attributable to poor temperature control in this run, for which the limits were $\pm$ 0.5 deg C.

As for the benzoyl peroxide, the decomposition of lauroyl peroxide at temperatures below its melting point showed a sigmoid variation with time and was accompanied by progressive melting. The degree of decomposition at which the presence of liquid phase was indicated by the particles sticking together is shown by S in Figs 1 and 2, and the point of complete liquefaction by L; the maximum rate of decomposition occurred near the point of complete liquefaction.

The initial stages of the decomposition below the melting point were more complex than for benzoyl peroxide. Thus at 47°C and above, there was a small, initial, and relatively fast, decomposition which decayed to give a 'plateau' in the decomposition curve before any obvious melting occurred. (It was, however, noticed that the peroxide particles became slightly translucent towards the end of this period). This behaviour is similar to, although much more pronounced than, that observed by Morsi[4] for the decomposition of benzoyl peroxide in vacuo at temperatures above its melting point.

At 40°C an additional, and very slow, initial stage appeared before the early fast stage noted above. At this temperature the above 'plateau' was approached after about three months and at about 20 per cent decomposition without melting. In general, the 'plateau' occurred at a greater extent of decomposition the lower the temperature.

At temperatures above the melting point, i.e. at 60°C and 70°C, the decomposition started at a high rate, which decreased fairly steadily with time. This is shown in Fig. 3 for decomposition at 70°C.

Decomposition of the peroxide in the deep 'layers' of small diameter, 4 mm, was faster than in the shallow layers, 14 mm diameter, at 47°C (Fig. 1). However, compared with the effect of increasing the sample depth on the decomposition of benzoyl peroxide[1], the effect on lauroyl peroxide was small (see further below).

Constants for maximum rate

Owing to the greater complexity of the decomposition of the lauroyl peroxide, it was not possible to apply in its entirety the two-phase model found satisfactory for deriving rate constants for the decomposition of benzoyl peroxide[1] (see, however, next section). Here, therefore, the maximum rates of decomposition were determined simply as the maximum slopes of the smooth curves, drawn in Figs 1-3, in the neighbourhoods of the points of complete liquefaction. The values obtained are given in Table 1, which includes values at 47°C for decomposition in both the 14 mm and 4 mm diameter tubes.

Table 1

Maximum rates of decomposition of

lauroyl peroxide.

Temperature $^\circ$C	Maximum rate.s^{-1}
47	6.9×10^{-7} (14 mm)
	7.9×10^{-7} (4 mm)
50.5	1.6×10^{-6}
53	3.4×10^{-6}
60	2.3×10^{-5}
70	9.5×10^{-5}

The maximum rates in Table 1 represent the weight of peroxide decomposed per second in unit weight of the mixture of peroxide and decomposition products and, for the purpose of defining critical conditions for thermal explosion, may be regarded as rate constants for a hypothetical 'zero order' reaction (provided the heat of reaction is relatively high)[5,6].

An Arrhenius plot of the rate constants in Table 1 is given in Fig. 4. Although there are only two points for the decomposition at temperatures above the melting point, they diverge sufficiently from the line through the points for decomposition below the melting point to suggest that they fall on a different line.

The equation for the line drawn for decomposition below the melting point is

$$k = 10^{28.60} e^{-\frac{51,200}{RT}} \qquad (1)$$

where, as usual, k is the rate constant, T the absolute temperature and R the universal gas constant.

For decomposition above the melting point, the corresponding equation is

$$k = 10^{16.72} e^{-\frac{32800}{RT}} \qquad (2)$$

The apparent 'activation energy' for the hypothetical zero order reaction based on maximum rates at temperatures below the melting point, i.e. 51,200 cal/mole, is close to the corresponding value obtained for benzoyl peroxide[1], i.e. 50,500 cal/mole. At a given temperature, however, the maximum rate of decomposition of lauroyl peroxide below its melting point is of order 10^2 times that of benzoyl peroxide.

The apparent activation energy for decomposition above the melting point is within the range observed for the decomposition of organic peroxides in solution (28,000 - 39,000 cal/mole[7], with the lower values more common) as found, also, by Morsi[4] and Fine and Gray[8] for the decomposition of benzoyl peroxide; a frequency factor of order 10^{16} (equation 2) has also been observed for the decomposition of organic peroxides in solution[7].

Liquid phase decomposition

The final liquid-phase decomposition of benzoyl peroxide at temperatures below its melting point has been found to obey a first order rate equation[1] and it is of interest to note that lauroyl peroxide behaves similarly. This is shown in Fig. 5, where the fraction of residual peroxide (i.e. 1-x), plotted logarithmically, is seen to decrease linearly with time for the final stage of decomposition at 53°C. The same behaviour was observed at 50.5°C and 47°C.

At temperatures above the melting point, however, the same semi-logarithmic plot yielded a graph of the form shown in Fig. 6 for the decomposition at 70°C. The straight line drawn through the results for the later stages of the results in Fig. 6 has an intercept of 0.70 at zero time; for the results at 60°C, the corresponding intercept was 0.82.

The gradients of the lines in Figs 5 and 6 yield values for first order rate constants for the corresponding decomposition ranges. These are plotted against the reciprocals of the absolute temperatures in Fig. 7 for all the available results, k_1 denoting first order rate constants for the initial stage of the decomposition above the melting point and k_2 the rate constants for the final stage at temperatures both above and below the melting point.

It will be seen that the final liquid phase decomposition at temperatures below the melting point is consistent, in terms of an overall first order rate process and Arrhenius temperature dependance, with the later stage of the liquid phase decomposition at temperatures above the melting point. This contrasts with the behaviour of benzoyl peroxide for which there were marked differences above and below the melting point[1,8]. Values of k_1 in Fig. 7 are about twice the values of k_2, while the apparent activation energy corresponding to the latter is 31,800 cal/mole, i.e. very nearly the same as for k_1 (equation 2). There seems to be no straightforward explanation for these findings in terms of decomposition mechanism, but this is outside the scope of the present work.

In terms of the model based on the assumption of quasi-equilibrium between the solid and liquid phases,[1,9] the maximum rate of decomposition occurs at the point of disappearance of the solid phase, i.e. the maximum rate is given by

$$\left(\frac{dx}{dt} \right)_{max} = k_2 (1 - x_l) \tag{3}$$

where x is the fraction decomposed in time t, k_2 the liquid phase rate constant for the two phase decomposition and x_l the degree of decomposition at which solid phase disappears.

Estimating x_l as the mean between an experimental point L in Figs 1 and 2 and the experimental point immediately preceeding it, and using the values of k_2 in Fig. 7, maximum rates of decomposition have been calculated from equation (3) and plotted in Fig. 4 for comparison with the values obtained above. In spite of the obvious inaccuracies in their derivation it will be seen that the maximum rates of decomposition obtained in the two different ways are in good agreement.

This agreement lends support to the two-phase decomposition model. The main difficulty in applying it fully here, and in deriving an equation to represent the important intermediate stage of the decomposition when two phases are present, is the complexity of the initial stages and consequent difficulty of assigning a suitable rate equation to the solid phase decomposition.

Induction period

As for benzoyl peroxide, the times to the maximum rate of isothermal decomposition of lauroyl peroxide at temperatures appreciably below the melting point are long, and it is these times which will effectively determine the induction periods for thermal explosion[6].

The times to maximum rate, or induction periods, are plotted logarithmically against the reciprocals of the absolute temperatures in Fig. 8. In spite of the complexity of the early stages of the decomposition the graph of Fig. 8 can evidently be used for linear interpolation and, limited, extrapolation.

The induction period for the decomposition, or explosion, of lauroyl peroxide varies even more rapidly with temperature than that of benzoyl peroxide. Thus, the apparent activation energy yielded by the results in Fig. 8 is 120,000 cal/mole which is about twice the corresponding value for benzoyl peroxide.

It was evident from the study of benzoyl peroxide[1], that the large induction periods and the large apparent activation energy were associated with the solid phase decomposition. The same, doubtless, applies to the decomposition of the lauroyl peroxide. It is outside the scope of this paper to discuss these effects but, briefly, it is interesting to note that the high activation energies widely observed for the decomposition of organic solids are associated with the slowness, and high activation energy, of molecular diffusion in the crystal and consequent powerful 'cage effect'[10].

The very slow solid phase decomposition observed for benzoyl and lauroyl peroxide occur at Tamman temperatures of about 0.9 and above. These are high compared with the value of about 0.5 at which decomposition usually becomes appreciable in ionic solids. Most of this difference may depend simply on the fact that, in crystals of organic compounds, lattice energies are low compared with activation energies for reaction but, to the extent that Tamman temperatures define corresponding physical states, the difference may also reflect greater restrictions on the mobility of the peroxide molecules, in the crystal lattice, imposed by their shapes.

HEAT OF DECOMPOSITION

A knowledge of the heat of decomposition of the lauroyl peroxide is required for the purpose of estimating the critical conditions for thermal explosion. Comparatively little is known about the decomposition mechanism of lauroyl peroxide but, by analogy with benzoyl peroxide, the most highly exothermic process is likely to be that represented by the following equation:

$$C_{11}H_{23}.CO - O - O - CO.C_{11}H_{23} \rightarrow C_{22}H_{46} + 2CO_2$$
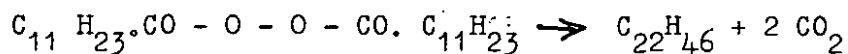
For present purposes it is sufficient to assume that the above is the sole decomposition reaction. Estimating the heats of formation of lauroyl peroxide and of the docosane by either the group contribution method of Franklin[11] or the bond contribution method of Benson and Buss[12], the heat evolved in the above reaction may be estimated as 78 kcal/mole, or 196 cal per gram of lauroyl peroxide decomposed.

THERMAL EXPLOSION

Containers (reagent bottles, drums etc) commonly have the form of circular cylinders with a height to diameter ratio of about 1.5. The critical diameter, D, for thermal explosion of an unstable compound in a container of this form and at an ambient temperature of T_o °K is given by

$$D = 2 \left[\frac{2.3}{Qk(T_o)} \cdot \frac{RT_o^2}{E} \cdot \frac{\lambda}{\rho} \right]^{\frac{1}{2}} cm \qquad (4)$$

where

Q = heat of reaction. cal/g

$k(T_o)$ = rate constant at temperatures T_o °K. s^{-1}

R = universal gas constant = 2 cal $mole^{-1}$ deg K^{-1}

E = activation energy, cal/mole

ρ = density g/cm^3

λ = thermal conductivity cal cm s^{-1} deg K^{-1}

The constant 2.3 applies to the situation for which heat transfer between the container surface and the atmosphere is high enough for the surface temperature to remain substantially equal to that of the atmosphere during the induction period for explosion. Where this is not so, the constant will be smaller.

By analogy with benzoyl peroxide[6] the ratio λ/ρ may be taken as 3×10^{-4} for lauroyl peroxide, then inserting the above estimated heat of decomposition, the activation energy from equation (1) and the appropriate values of $k(T_o)$ from Fig. 4, the following estimates of critical diameter for thermal explosion of cylindrical containers (of the above form) of lauroyl peroxide may be obtained:-

Ambient Temperature °C	Critical diameter cm	Time to explosion
50	6	4 days
45	11	3 months
40	21	$5\frac{1}{2}$ years

The times to explosion in the above table have been estimated from Fig. 8.

The above estimates make no allowance for the effect of possible quenching of incipient explosion by melting and gas evolution. Observations on the thermal explosion of benzoyl peroxide[6] indicate that this can increase the critical ambient temperature for explosion of a given size by at least 3 deg C.

PRACTICAL IMPLICATIONS

The above estimates of critical diameter increase by a factor of about two for a decrease of 5 deg C in ambient temperature, while the induction period increases rapidly to very large values as the ambient temperature falls below 50°C. While the critical sizes are small enough to indicate, on their own, the existence of a thermal explosion hazard under normal conditions of storage and transport, the estimated induction periods imply that a hazard could only, in fact, arise under special circumstances.

For example, repeated exposure to daytime peak temperatures of the order of 50°C, or higher, such as can easily be encountered in parts of a ship's hold or on the surface of a package exposed to the sun on deck, in the tropics and in areas such as the Persian Gulf[13], could reduce the "chemical" part of the induction period to zero within a period of the order of days. The residual thermal induction period for explosion, as estimated from the calculations of Zinn and Mader[14,6], for, say, the 6 cm package at an ambient temperature a few degrees above the critical value, will then be of the order of 5 hours, i.e. a period during which the surface temperature of a package could be near its daytime peak value for most of the time. In periods of this order, the temperature of surfaces exposed to the sun can, in fact, be considerably above the melting point of lauroyl peroxide (54°C).

Carriage of lauroyl peroxide as deck cargo protected from the direct influence of solar radiation, as is in fact required by shipping regulations[15], and the provision of outer packing material (in which, with a thermal diffusivity typically of order 10^{-3} cm^2 s^{-1}, the amplitude of a 24-hourly surface temperature cycle can be halved at a depth of about 4 cm) should ensure that the temperature of the peroxide will usually remain near to prevailing mean shade temperatures. The mean values encountered on board ship appear unlikely anywhere to exceed 35°C for periods of the order of a few days[13] so that, under these conditions, carriage of the peroxide should be safe - with a margin of at least 10 deg C to allow for unusual conditions.

From the point of view of freedom from risk of thermal explosion, the above considerations show that lauroyl peroxide is a somewhat borderline case in which the existence of a large induction period makes a major contribution to the safety. The approximate calculations confirm that the relatively simple precautions in the shipping regulations are sufficient for the safety of transport by sea. It is understood that lauroyl peroxide has, in fact, been carried on board ship without incident for many years through the Red Sea - where it is estimated[13] that mean shade temperatures of $35^{\circ}C$ might be encountered for a few days in port.

The above considerations will also apply to storage on land. However, such storage may be quite prolonged and, accordingly, the margin of safety may be considerably reduced in hot localities. Where storage in hot localities is contemplated or where, in any process, lauroyl peroxide is likely to be exposed to moderately elevated temperatures, a more precise assessment of the explosion behaviour should be made - preferably based on experimental determination of the critical explosion conditions.

The risk of thermal explosion will need to be considered with special care if there is ever a need to mix lauroyl peroxide in large quantities with a plasticiser. By analogy with the behaviour of mixtures of benzoyl peroxide and plasticisers[2], the induction period for isothermal decomposition could then be zero and the critical sizes for thermal explosion at given temperatures could be even less than have been predicted above for the "pure" lauroyl peroxide.

ACKNOWLEDGMENT

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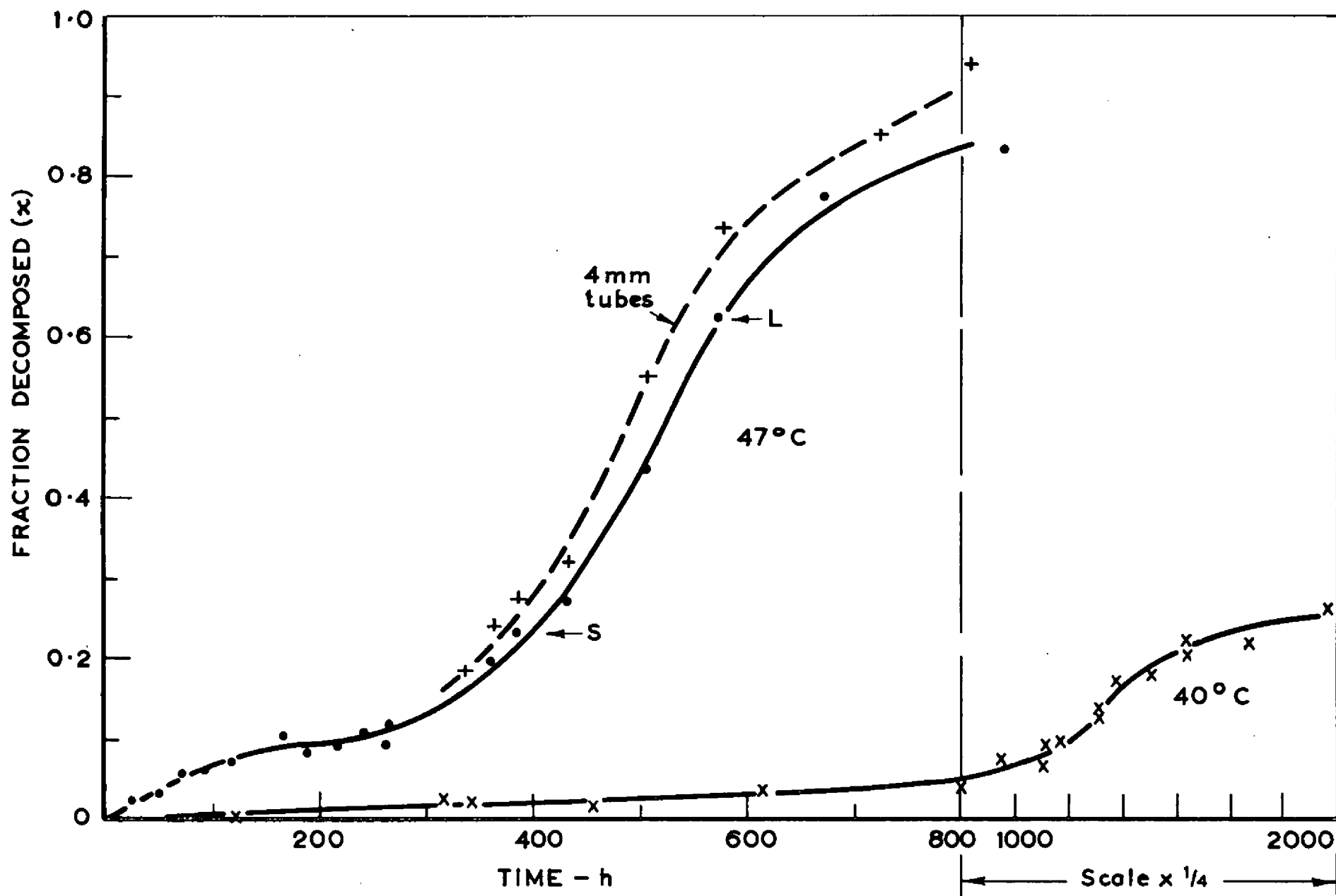   H.M. Stationery Office.

FIG.1. DECOMPOSITION OF LAUROYL PEROXIDE AT 40°C AND 47°C
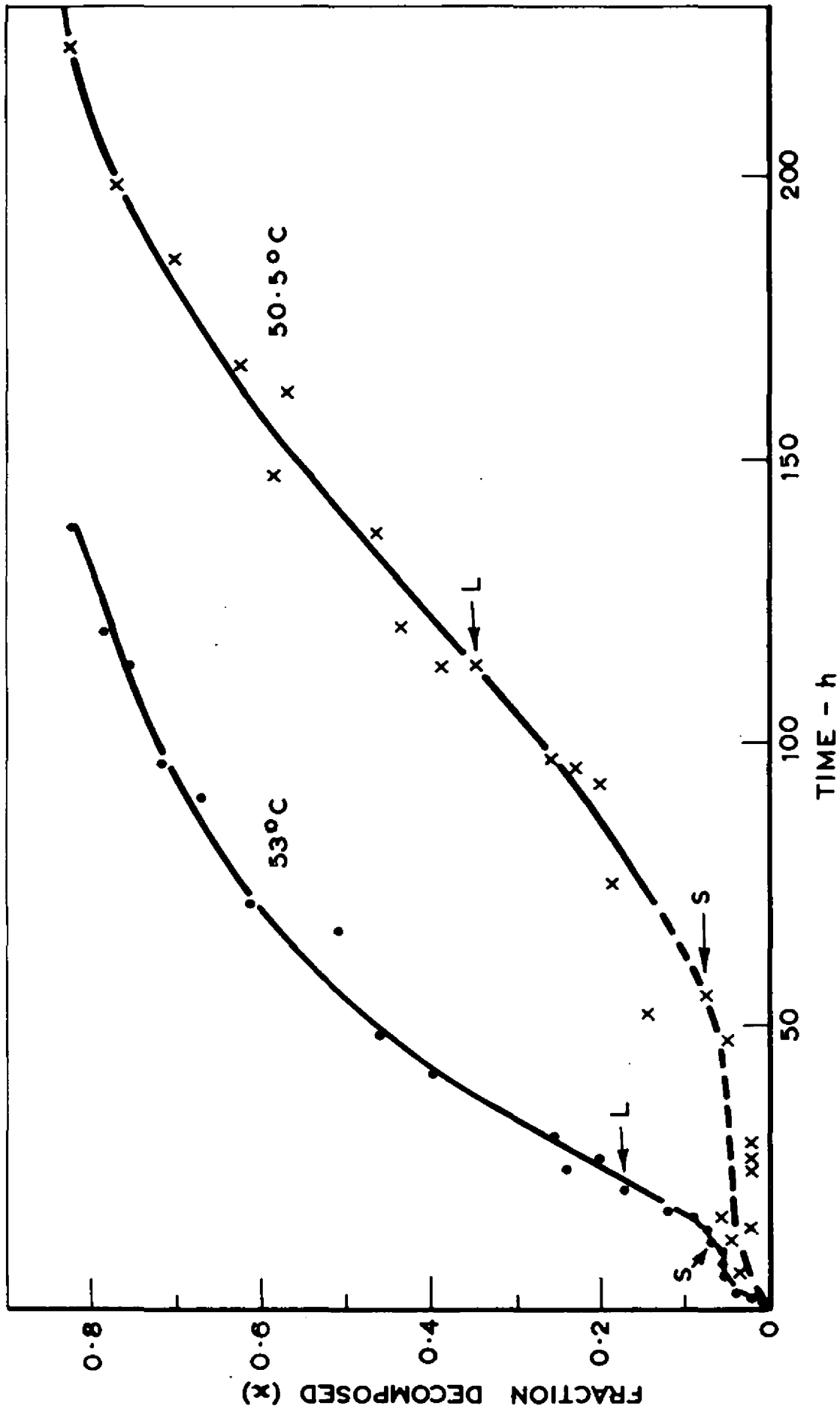(including results for decomposition in 4mm tubes)

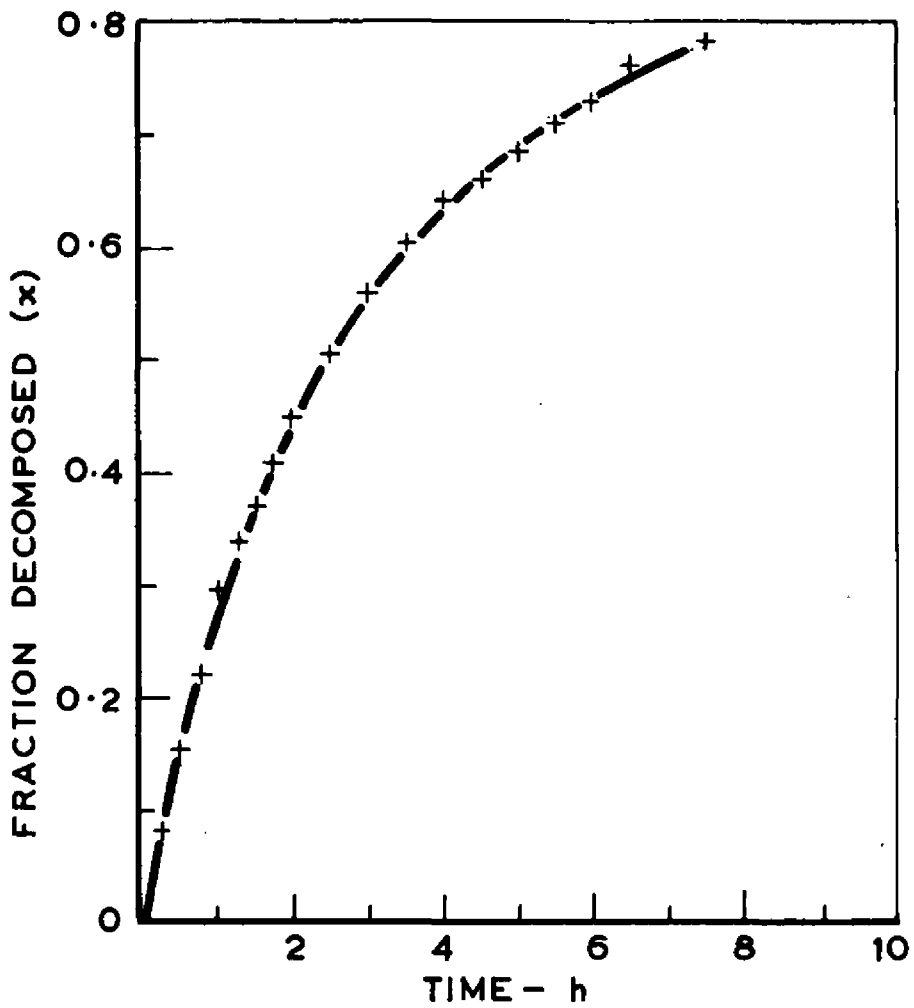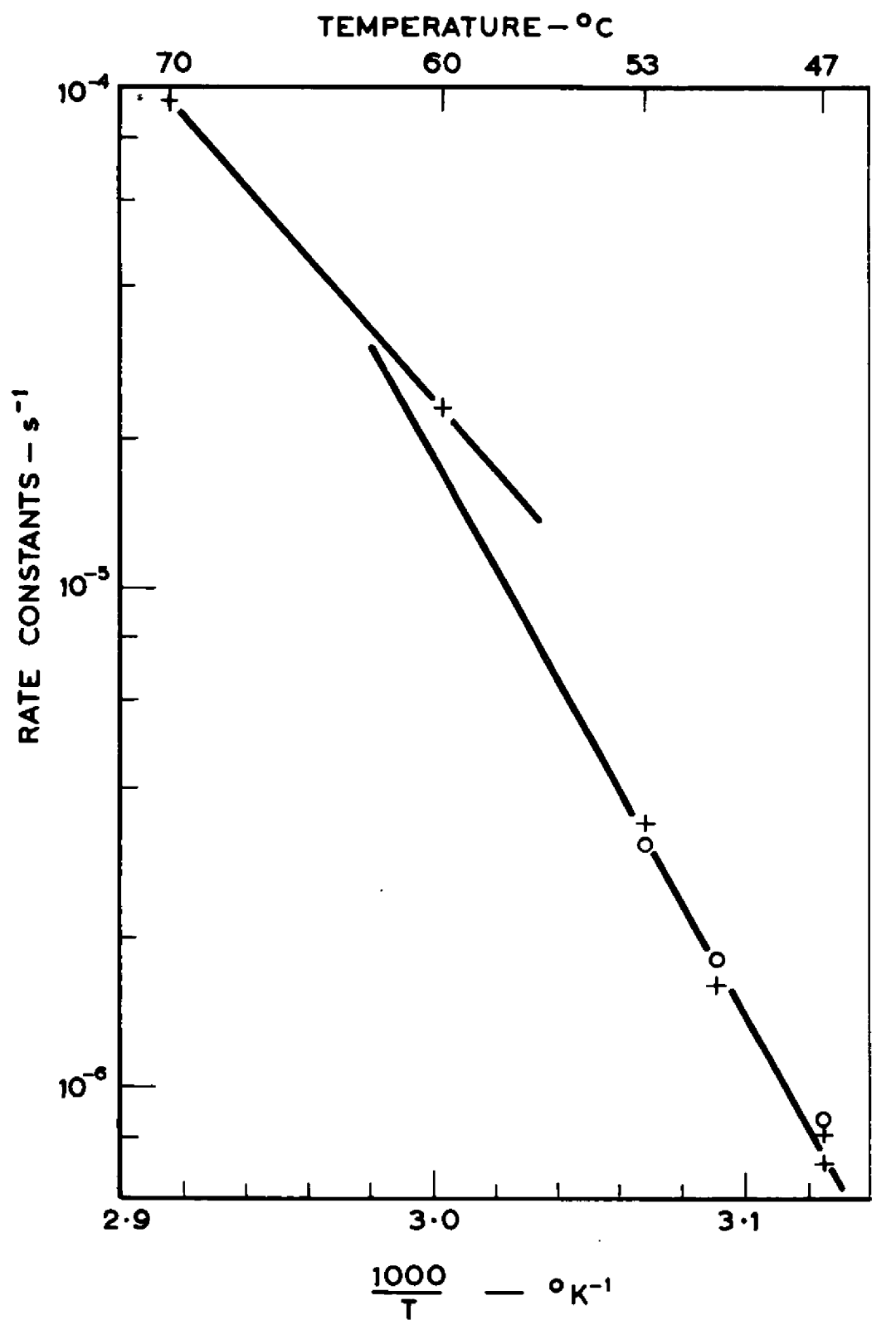FIG. 2. DECOMPOSITION OF LAUROYL PEROXIDE AT 50·5°C AND 53°C

1/8047

FIG. 3.   DECOMPOSITION OF LAUROYL
PEROXIDE AT 70° C

TEMPERATURE – °C

RATE CONSTANTS – s⁻¹

$$\frac{1000}{T} \quad - \quad °K^{-1}$$

+ – From maximum gradients of decomposition curves

o – From equation 3
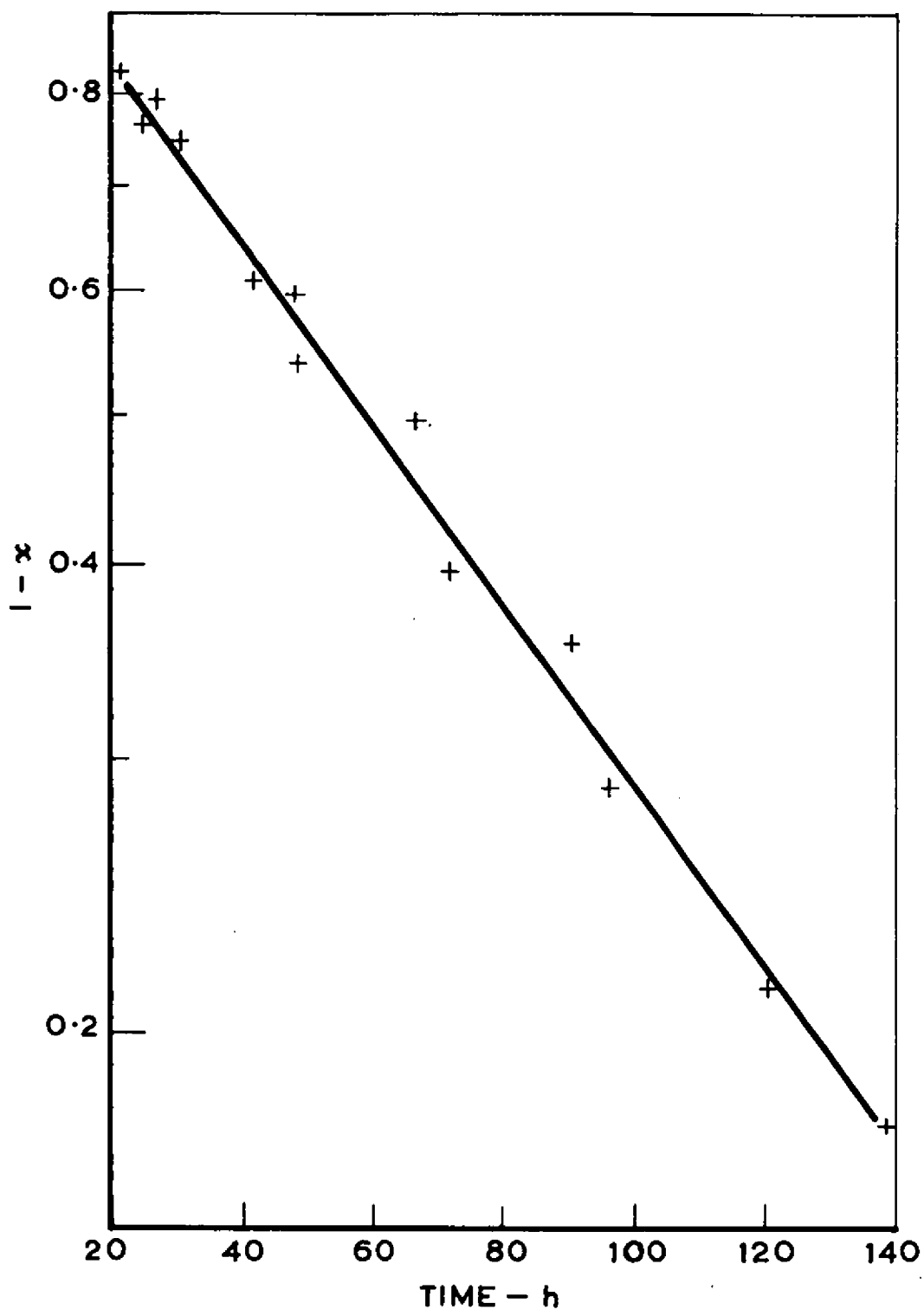
FIG. 4.   RATE CONSTANTS AT MAXIMUM RATE OF DECOMPOSITION

FIG. 5.   LIQUID   PHASE   DECOMPOSITION-53°C

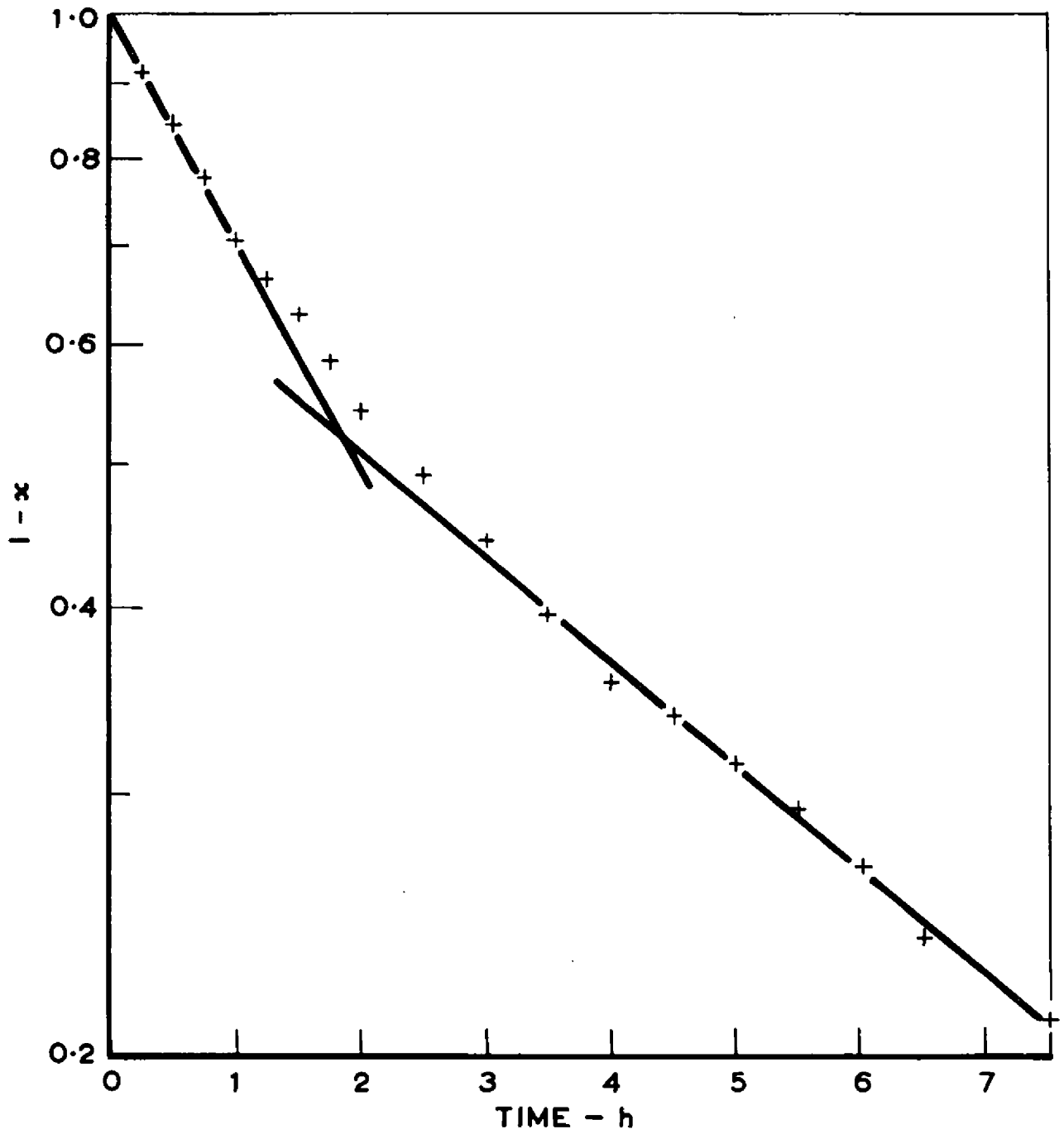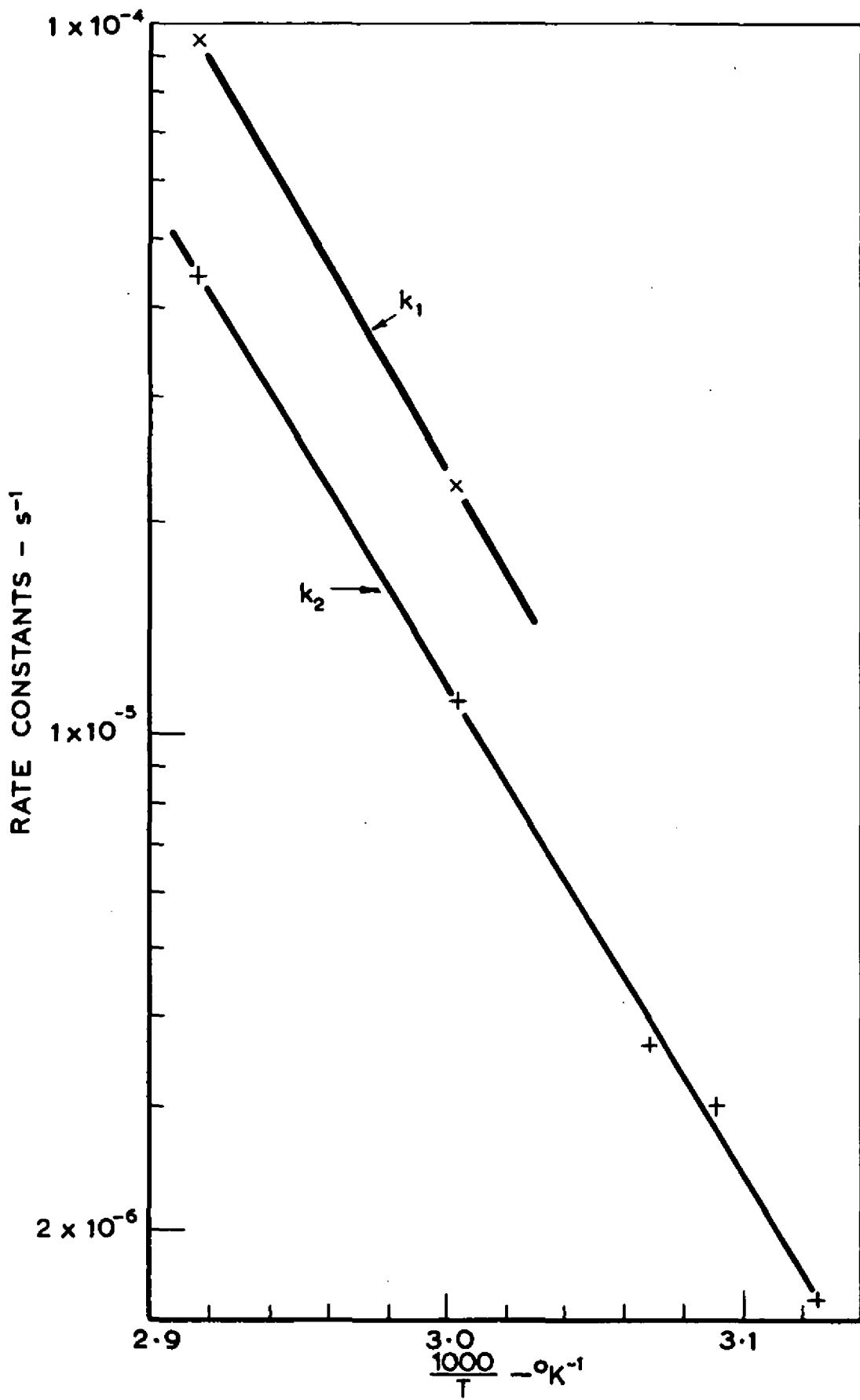FIG. 6.   LIQUID   PHASE   DECOMPOSITION—70°C
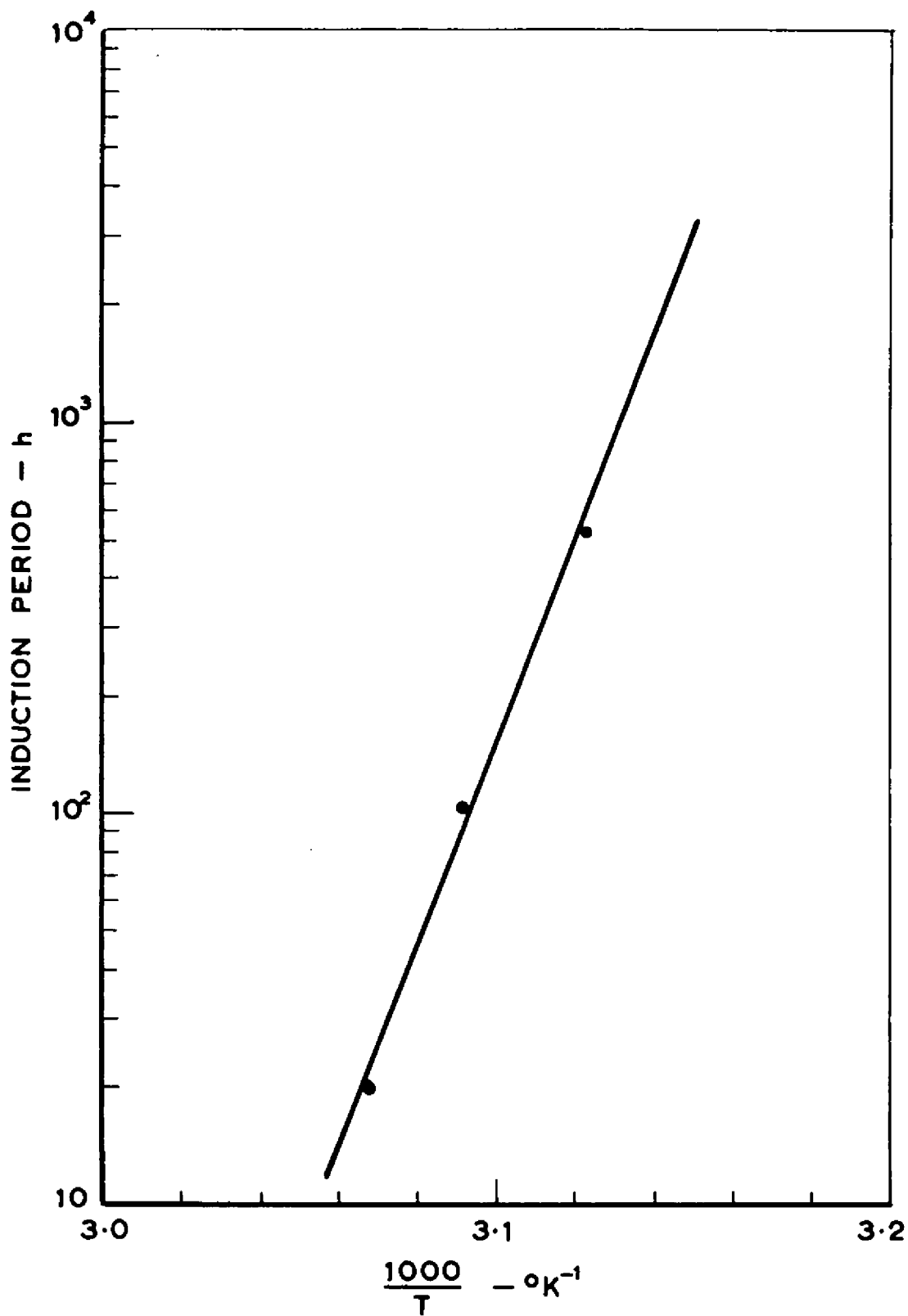
FIG. 7.   RATE CONSTANTS FOR LIQUID PHASE

FIG. 8. INDUCTION PERIODS FOR DECOMPOSITION
AT MAXIMUM RATE