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THE THERMAL DECOMPOSITION OF BENZOYL
PEROXIDE PASTES

by

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SUMMARY

Effective reaction kinetics are determined for the thermal decomposition of benzoyl peroxide in the form of pastes with plasticisers.

The implications of the results for the occurrence of thermal explosion in the pastes are indicated briefly.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE

JOINT FIRE RESEARCH ORGANIZATION

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INTRODUCTION

Benzoyl peroxide is commonly marketed and used in the form of a paste with various plasticisers. These pastes are relatively insensitive to initiation by friction and impact and in these respects are safer to handle than the pure peroxide.

This note is concerned with the behaviour of benzoyl peroxide pastes exposed to moderately elevated temperatures. An account is given of the decomposition of the peroxide at different temperatures and with different concentrations of the common plasticisers dimethyl phthalate and tritolyl phosphate.

The results described have been obtained primarily as an adjunct to a study of the thermal explosion of benzoyl peroxide paste (to be reported elsewhere).

EXPERIMENTAL

As in earlier studies of benzoyl peroxide[1] the decomposition of the peroxide paste was followed by the assay of residual peroxide[2] in samples of 0.2 g heated for different periods at a given temperature.

In order to avoid the difficulties of handling the thick pastes quantitatively, the "pastes" were prepared by adding the requisite quantity of plasticiser to 0.2 g samples of the dry peroxide (98 per cent purity) by means of a micro-pipette. A few comparative tests were made, however, with a paste of commercial origin.

The samples of paste were heated in test-tubes of 14 mm diameter in which the depth of sample was about 5 mm at the centre. As a check on the possibility of a significant loss of volatile products (previously noted for the dry peroxide in layers of this depth[1]) some tests were made on the same weight of paste in tubes of 4 mm diameter, in which the depth of sample was about 24 mm.

RESULTS

Dimethyl phthalate pastes

The effect of the concentration of plasticiser was determined only for pastes of peroxide with dimethyl phthalate (DMP) and is shown in Fig.1 for decomposition at 80°C. The following points may be noted:-

(a) Commercial pastes commonly contain 35-50 per cent of DMP and, at these concentrations, the rate of decomposition at 80°C decays steadily from a relatively high initial value.

(b)   There is no difference between the behaviour of the prepared "pastes" containing 35 per cent of DMP and samples of a commercial paste of the same composition.

(c)   Increasing the depth of sample for paste containing 35 per cent of DMP makes no difference to the course of decomposition at 80°C and it is concluded that there is no loss of volatile products of importance to the decomposition process in the shallow layers[1]. This may not be true at the lower concentrations of DMP, but these are not at the moment of practical importance and so the effect has not been examined further.

(d)   Pastes containing 5.6 per cent DMP showed a sigmoid decomposition/ time relationship similar to that observed for the dry peroxide, although the time to the inflexion, 15 hours, was one-third of that for the dry peroxide.

(e)   At the higher DMP concentration of 10.7 per cent the results were somewhat scattered, but it is clear that the similarity with dry peroxide has disappeared and the fractional rate of decomposition is substantially constant at least up to about 60 per cent decomposition.

At lower temperatures, the fractional rate of decomposition of the pastes containing 35 and 50 per cent DMP was constant up to 40–60 per cent decomposition; this is illustrated in Fig.2 for the paste containing 35 per cent DMP at a temperature of 70°C.

In all cases, the decomposition of the peroxide was accompanied by the gradual disappearance of solid phase in the paste. The extent of decomposition at which the pastes became completely liquid is indicated approximately by L in Figs 1 and 2 for the different concentrations and temperatures shown. For DMP concentrations of 10.7 per cent and above, it was up to the neighbourhood of this point that the fractional rate of decomposition was constant; beyond it, the rate began to decrease.

Tritolyl phosphate pastes

Results for a paste of benzoyl peroxide with 35 per cent tritolyl phosphate (TTP) at 60 and 80°C are shown in Fig.3. As for DMP the fractional rate of decomposition was constant until about half the peroxide was decomposed. The initial fractional rate of decomposition of peroxide in TTP was 40 per cent of that for the corresponding paste in DMP at 60°C and 37 per cent at 80°C.

Effective reaction kinetics

For application to the problem of thermal explosion, we require the maximum value of the mass rate of decomposition of peroxide, dm/dt, per unit mass of paste.

Over any small change of concentration, the decomposition may, with sufficient accuracy, be regarded as of zero order. If x is the fraction of

peroxide decomposed in time t (as Figs 1-3), we then have

$$\left(\frac{dm}{dt}\right)_{max} = C_0\left(\frac{dx}{dt}\right)_{max} = k\ C_0 \qquad (1)$$

where C_0 is the initial concentration of peroxide in the paste on a mass basis, and the zero order rate constant, k, is the maximum gradient of the decomposition record for a given paste. For the pastes containing the higher proportions of plasticiser, the reaction has, in fact, been found to be of zero order up to 40-60 per cent decomposition.

The maximum values of dm/dt are thus the initial values for the pastes containing the higher proportions of plasticiser, and the value at the inflexion of the decomposition record for the paste containing 5.6 per cent DMP. The way in which the maximum mass rate of peroxide decomposition depends on the proportion of dimethyl phthalate in pastes at 80°C is shown in Fig.4. The value for the pure peroxide is derived from previous results[1] and corresponds to about 50 per cent decomposition, the peroxide then being diluted with products (as previously[1], the loss of carbon dioxide is ignored in these calculations).

The rate constants obtained for the initial decomposition of the pastes containing 35 and 50 per cent plasticiser are plotted logarithmically against the reciprocals of the corresponding absolute temperatures in Fig.5.

The comparable "zero order" rate constants for the dry peroxide are also shown in Fig.5. These are obtained from the equation

$$k = \left(\frac{dx}{dt}\right)_{max} = K_{obs}(x_l + \underline{a})$$

where K_{obs} and $\underline{a}$ are functions of the rate constants for the solid and liquid phase reactions and of the phase compositions, and x_l is the degree of decomposition at which solid phase disappears. The origin and status of this equation are dealt with in reference 1.

The equation for the straight line drawn through the points for the paste containing 35 per cent DMP is

$$k = 10^{26.2}\ e^{\frac{-49300}{RT}}\ s^{-1}$$

Within the limits of the experimental error, the apparent activation energy, 49300 cal/mole, is the same for all three pastes and the dry peroxide.

DISCUSSION

a. Effective reaction kinetics

The effective reaction kinetics for the decomposition of the benzoyl peroxide pastes are simple and, for the purposes of this note, require no detailed discussion. There are, however, a few qualitative features that merit brief comment.

As indicated, the course of the decomposition of the paste containing the lowest concentration of dimethyl phthalate, 5.6 per cent, is similar to that of the dry peroxide. It has previously been shown[1] that the autocatalytic character of the decomposition of the dry peroxide can be accounted for largely quantitatively by the accumulation of a liquid phase, in near-equilibrium with the solid, as the decomposition proceeds - (the rate of decomposition in the liquid phase being greater than in the solid phase) and a similar process no doubt occurs in pastes containing very low concentrations of plasticiser. At the higher concentrations of plasticiser, however, similarity with the decomposition of dry peroxide disappears and the above model is inapplicable.

It will be seen from Fig.4 that, at 80°C, the maximum rate of decomposition of peroxide in the paste containing 35 per cent DMP is about 4 times the corresponding rate for the initially pure peroxide. It has been estimated[1] that during the decomposition of the pure peroxide at 80°C the rate of decomposition in the liquid phase is about 6 times the rate in the solid phase when both phases are present together. If the rate of decomposition of the solid phase is the same in both systems, it can be estimated that the rate of decomposition of peroxide in the liquid phase of the paste at 80°C is about 27 times the rate in the solid. At lower temperatures the ratio of the rates increases[1] and, generally, it seems that most of the measured decomposition of peroxide in pastes containing the higher proportions of plasticiser occurs in the liquid phase.

The higher absolute rate of peroxide decomposition in the liquid phase of the pastes rich in plasticiser makes it less likely that the earlier assumption[1] of near equilibrium between the liquid and solid phases is applicable to these pastes. It is more probable that the rate of decomposition in the liquid phase will be partly governed by a commensurate rate of mass transfer of peroxide from the solid to the liquid. This could account for the observed absence of acceleration of the decomposition as the liquid phase increases in amount and solid disappears.

b. Thermal explosion

Application of the results in this paper to the thermal explosion of benzoyl peroxide pastes will be discussed in detail elswhere in conjunction with the results of actual explosion experiments. Provided, however, it may be assumed realistically that there is no large difference in the heat of reaction for the decomposition of benzoyl peroxide in the pure state and as a paste with plasticiser, some pertinent conclusions can be drawn immediately from the above results when considered in relation to the known explosion behaviour of the pure peroxide[3].

It is apparent from Fig.5 that the ratios of the maximum rates of decomposition of the pastes to that for the dry peroxide are constant; as indicated above, it is about 4, on the mass basis, for the paste containing 35 per cent dimethyl phthalate. Further, the induction period for the decomposition of the dry peroxide, already 450 hours at 70°C (about 19 days) increases by a factor of about 10 for a decrease in temperature of 10°C. These facts imply that a risk of thermal explosion may exist for the peroxide pastes at temperatures at which, for practical purposes, it is absent for the dry peroxide.

Specifically, it may be inferred from well-known thermal explosion theory[4], that for the paste containing 35 per cent DMP, for example, the critical size for thermal explosion in a given environment will be less than that for the dry peroxide by a factor of $1/\sqrt{4}$, i.e. 0.5.

The foregoing considerations are sufficient to indicate that the thermal explosion of benzoyl peroxide pastes may be of practical importance and that, consequently the conditions for its occurrence need to be determined quantitatively.

It is evident from Fig.4 that if there is, in fact, a practical risk of thermal explosion in benzoyl peroxide pastes containing, say, 35 or 50 per cent DMP, the risk may be reduced by reducing the concentration of DMP; however, this must be balanced against a possible increase in sensitivity to impact and friction. At a plasticiser concentration of 35 per cent, a change of plasticiser from dimethyl phthalate to tritolyl phosphate will reduce the rate of decomposition by a factor of $2\frac{1}{2}$; this also provides a means of controlling the risk of thermal explosion.

ACKNOWLEDGMENT

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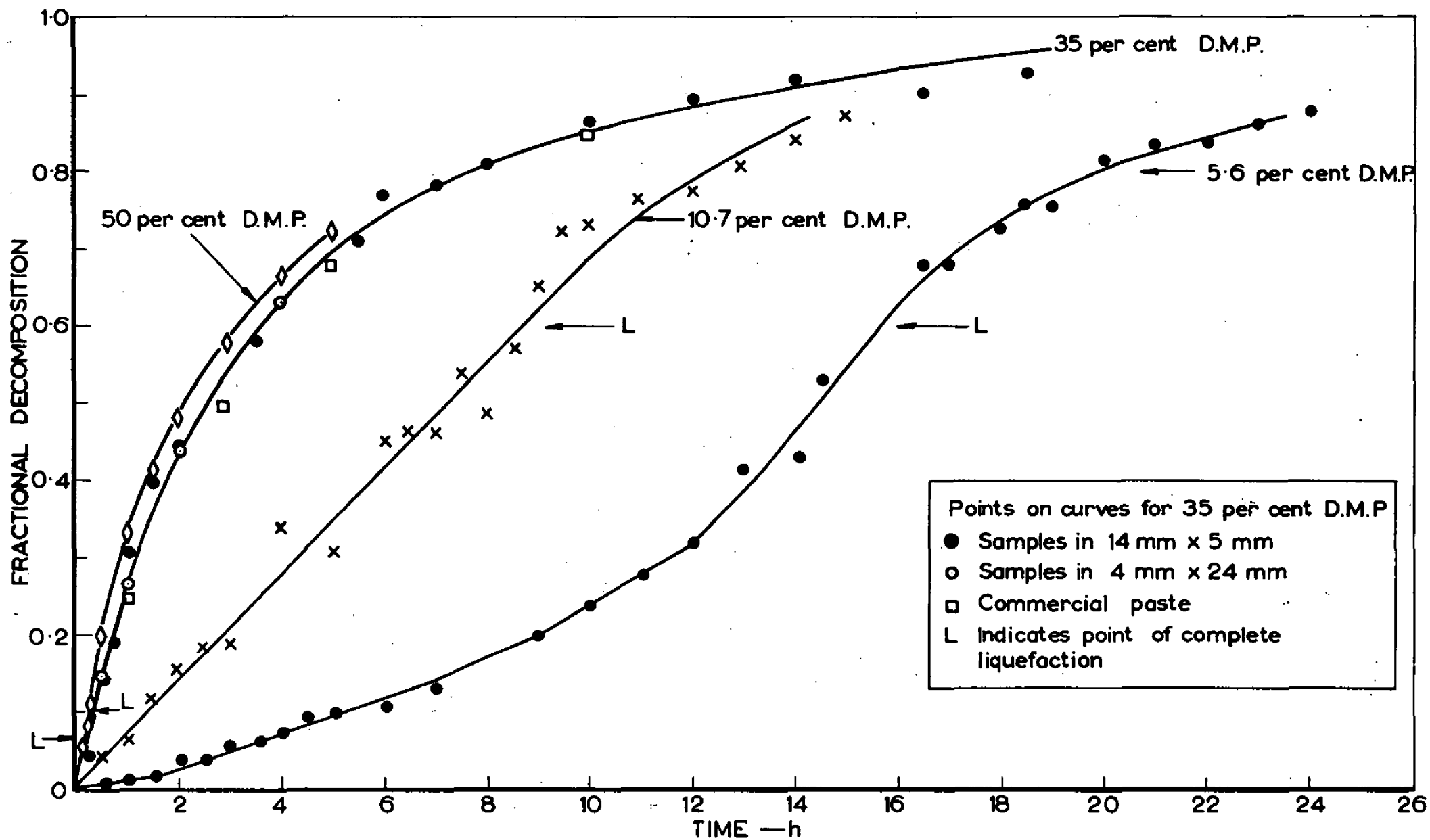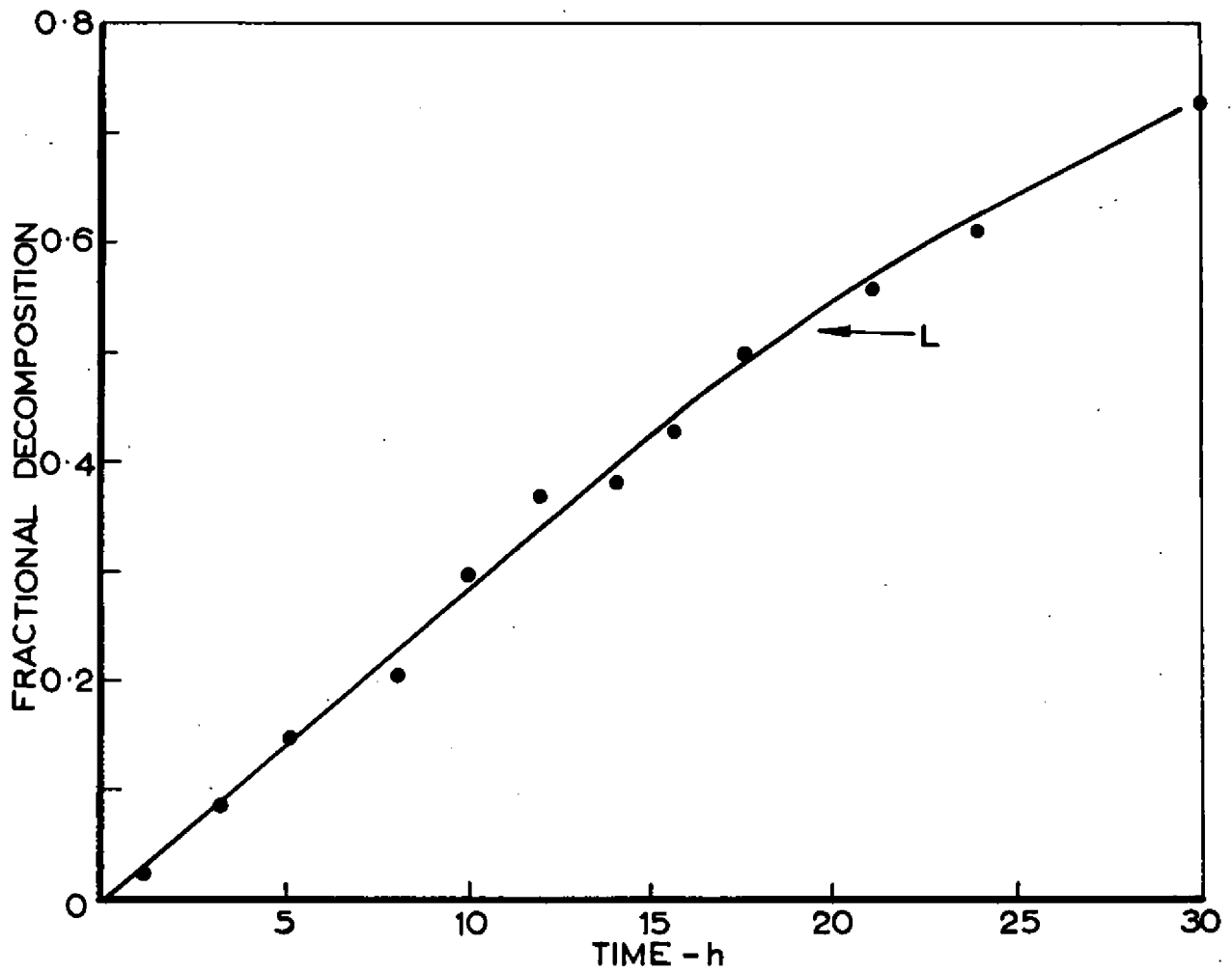
FIG. 1. DECOMPOSITION OF BENZOYL PEROXIDE PASTE WITH DIMETHYL PHTHALATE (D.M.P AT 80°C

L Indicates point of complete liquefaction

FIG. 2. DECOMPOSITION OF BENZOYL PEROXIDE PASTE
WITH 35 PER CENT DIMETHYL PHTHALATE
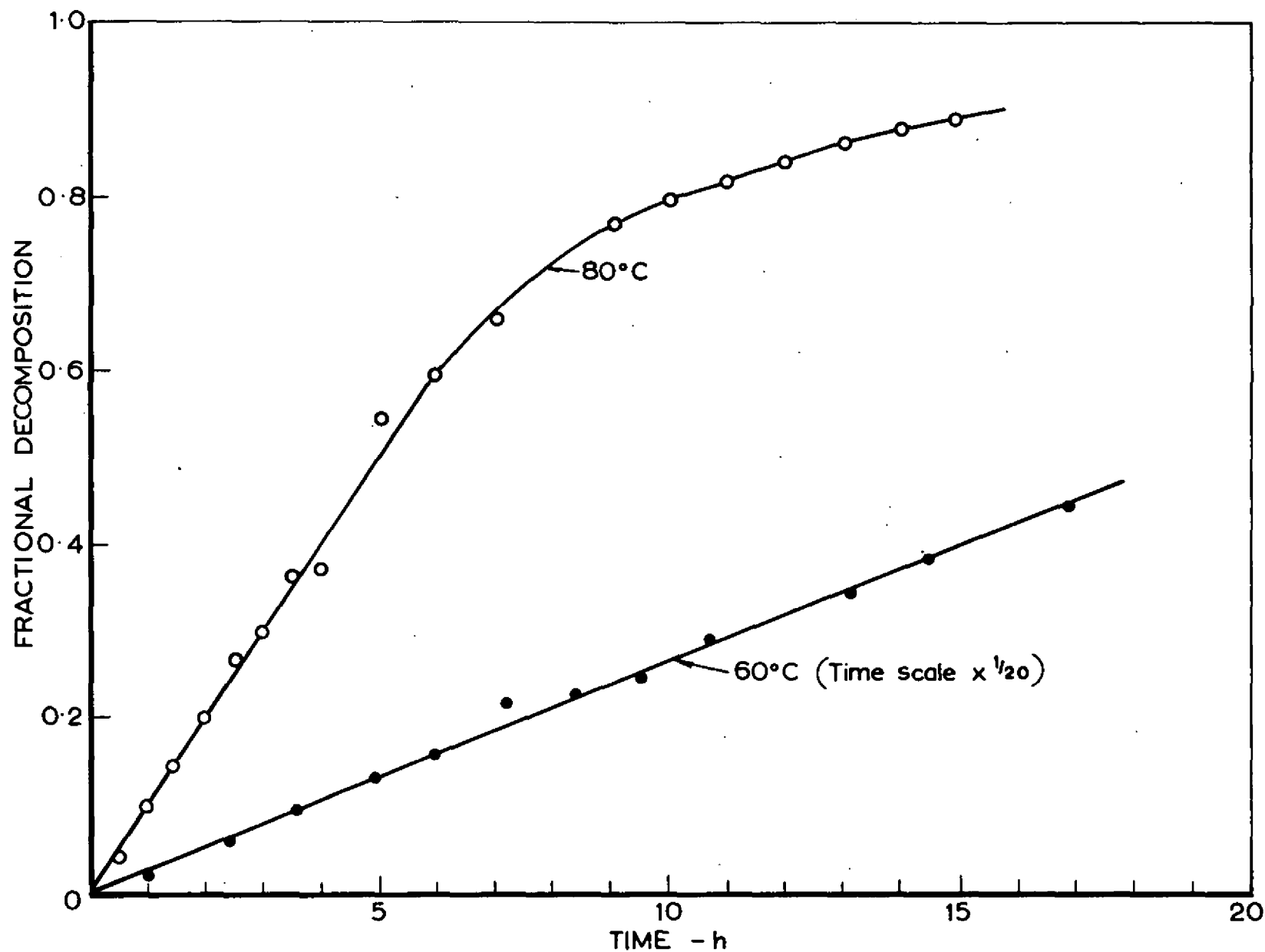(D.M.P.) AT 70°C

FIG. 3. DECOMPOSITION OF BENZOYL PEROXIDE PASTE WITH 35 PER CENT TRITOLYL PHOSPHATE
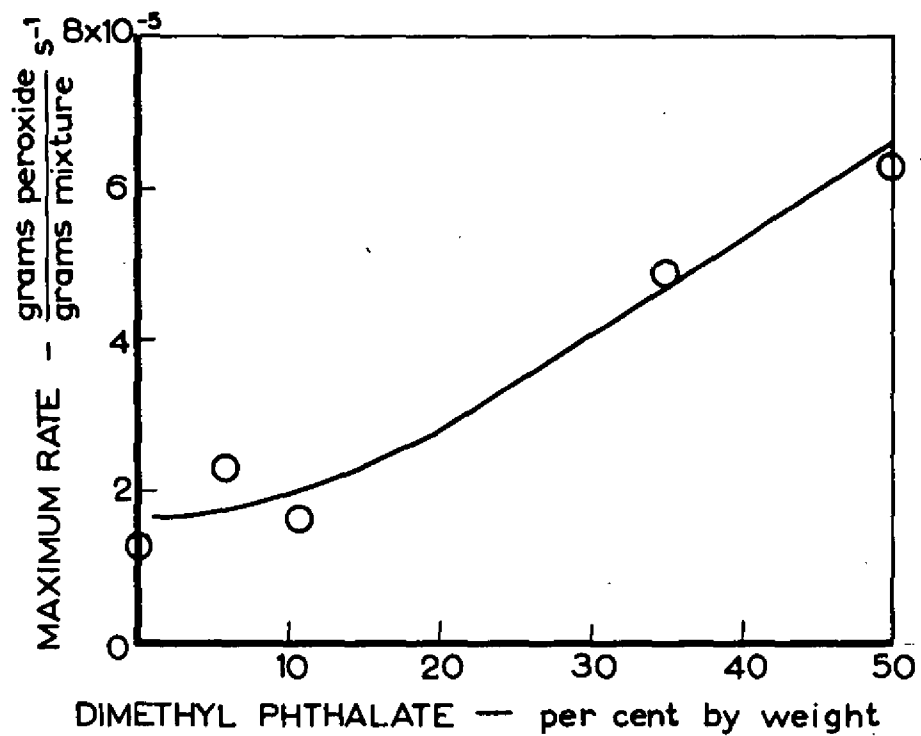
FIG. 4. MAXIMUM RATE OF PEROXIDE DECOMPOSITION
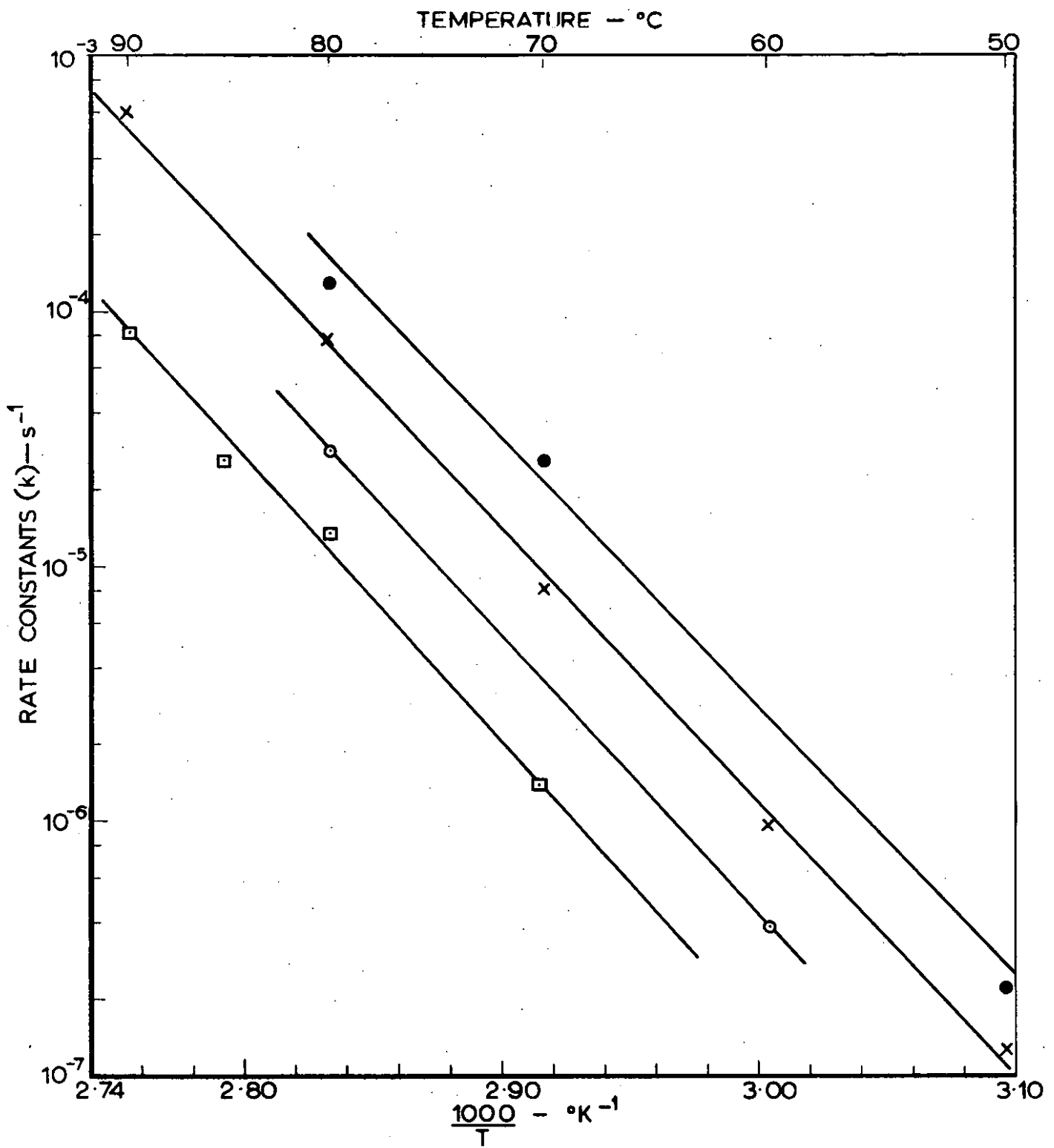AGAINST COMPOSITION OF PASTE

FIG. 5. RATE CONSTANTS FOR THE DECOMPOSITION OF BENZOYL PEROXIDE PASTES