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A TRACER STUDY OF THE BENZOYLOXY RADICAL

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Abstract—The behaviour of benzoyloxy radicals in solution at 60° has been examined by tracer methods. Benzoyl peroxide labelled with carbon-14 has been used as the source of the radicals. It has been shown that the proportion of radicals losing carbon dioxide depends upon the nature of the solvent and the concentration of peroxide and that in certain cases almost all the radicals dissociate before they can engage in other reactions. The effects of diphenylpicrylhydrazyl and thiophenol upon the reactions of the benzoyloxy radicals have been examined. From the rate of production of carbon dioxide, it is possible to measure the rate of decomposition of the peroxide. The relationship between the overall rate of decomposition and the rate of dissociation of the peroxide is discussed. New evidence is presented concerning the nature of the initiation process in the induced decomposition of the peroxide. It is concluded that the velocity constant for the dissociation of benzoyl peroxide to benzoyloxy radicals at 60° is about $1{\cdot}5 \times 10^{-6}\ \mathrm{sec}^{-1}$.

Several papers[1] have already been published concerning detailed studies of the initiation reactions when benzoyl peroxide is used as sensitiser for the polymerisation of unsaturated compounds. The work has involved the use of benzoyl peroxide labelled with carbon-14. It has been shown that tracer methods permit a direct study of the competition between the reactions:

$$C_6H_5{\cdot}CO{\cdot}O{\cdot} \longrightarrow C_6H_5{\cdot} + CO_2$$

$$CH_2{:}CH\,X + C_6H_5{\cdot}CO{\cdot}O{\cdot} \longrightarrow C_6H_5{\cdot}CO{\cdot}O{\cdot}CH\,X{\cdot}$$

This study is leading to fresh information on the factors governing the reactivities of molecules and free radicals. It has been pointed out that it is possible to determine the relative reactivities of various monomers towards the benzoyloxy radical, and also to investigate the effects of substituents upon the stability of this radical. To complete the study of benzoyloxy radicals formed by thermal dissociation of benzoyl peroxide, it is necessary to consider the behaviour of the radicals in an inert solvent; in this paper there is an account of an investigation of the decomposition of the peroxide in benzene. In addition, the effects of certain radical scavengers upon the behaviour of benzoyloxy radicals in benzene have been examined. Some observations have also been made concerning the reactions of benzoyloxy radicals in other solvents.

For the work described here, two types of labelled benzoyl peroxide were used; in the first, only the carboxyl carbon atoms were labelled, whereas in the second type the peroxide was labelled uniformly with carbon-14.

There have been many investigations concerning the nature of the products formed during the decomposition of benzoyl peroxide in solution, the latest being those of Lynch and Pausacker.[2] All the previous work has, of necessity, involved

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[1] J. C. Bevington, *Proc. Roy. Soc.* A **239**, 420 (1957)

[2] B. M. Lynch and K. H. Pausacker, *Aust. J. Chem.* **10**, 40 (1957).

solutions of quite high concentrations and in most cases the decompositions have been allowed to proceed almost to completion. Under these conditions the decomposition is complicated by secondary reactions, in particular a radical induced decomposition. This induced reaction can be eliminated by the use of very dilute solutions in inert solvents, and the tracer techniques used in the work described here allowed the use of such solutions. Most of the work was performed with benzoyl peroxide at a concentration of 0·5 g/l. but some experiments involved solutions containing only 0·05 g/l. These concentrations are similar to those which are used when the peroxide functions as an initiator for radical chain reactions. Further, it was necessary to use only 2 ml of solution in each experiment.

Although the main object of the work was to discover the fate of the benzoyloxy radicals, the behaviour of phenyl radicals formed from them was also studied. It is hoped to present the results of this part of the work in a second paper.

EXPERIMENTAL

Labelled benzoyl peroxide was prepared from [^{14}C]benzoic acid through benzoyl chloride; it was purified by precipitation with methanol from solution in chloroform. Samples of uniformly labelled and carboxyl-labelled benzoic acid were supplied by the Radiochemical Centre, Amersham. The specific activities of the uniformly and carboxyl-labelled peroxides were, respectively, approximately 45 and 28 μc/g of carbon.

Stock solutions of the labelled peroxides were made in benzene; measured volumes were introduced into break-seal tubes and then the benzene was sublimed off at low temperatures under vacuum. A reservoir on the vacuum line contained benzene and phosphorus pentoxide; the benzene had previously been dried over sodium and fractionated. From this reservoir, benzene was distilled on the vacuum line into the reaction tubes. The solutions were degassed completely and then the tubes were sealed. The tubes were kept at 60·0° for the required time. The concentrations in the reaction mixtures were measured at 20°.

Analyses for products formed during the decomposition of the peroxide were performed by the method of isotope-dilution analysis. In the case of carbon dioxide, the break-seal tube was attached to the vacuum line and the contents were frozen in liquid air. After the seal had been broken, a known weight of inactive carbon dioxide was condensed in the tube. The active and inactive carbon dioxide were mixed by repeated thawing and freezing of the contents of the tube and by distillation of the volatile contents from the reaction tube to a second tube on the vacuum line. The carbon dioxide was then allowed to evaporate at —78°. Isotope-dilution analysis for solid products was performed by mixing the reaction mixture with appropriate carrier material in solution. The solution was evaporated to dryness at low temperature, and then a pure sample of the material under examination was isolated by repeated crystallisation. Tests with labelled contaminants showed that the following methods were suitable for purification: for benzoic acid, three crystallisations from carbon tetrachloride; for phenyl benzoate, four crystallisations from ether.

All materials were assayed by gas counting, a mixture of carbon dioxide and carbon disulphide being used.[3] Solid samples were oxidised by the method of wet combustion.

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[3] J. C. Bevington, G. M. Guzman and H. W. Melville, *Proc. Roy. Soc.* A **221**, 437 (1954).

The method of calculation used in isotope-dilution analysis is well known, but mention must be made of a point in connexion with analyses for carbon dioxide produced from carboxyl-labelled peroxide. The specific activity of carbon dioxide produced during the decomposition of this type of labelled peroxide can be found only from that of the original peroxide; the specific activity, per g of carbon, for the carbon dioxide is seven times the corresponding quantity for the peroxide.

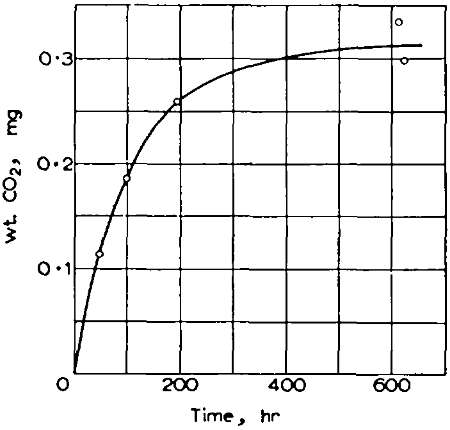

Fig. 1.

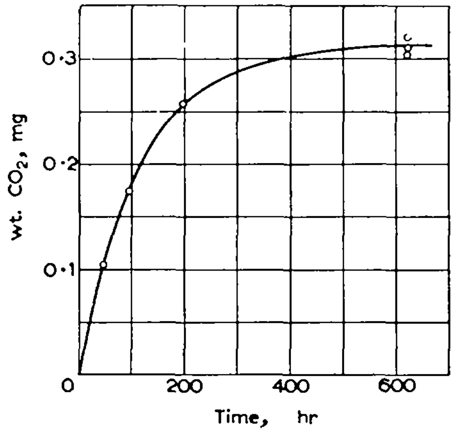

Fig. 2.

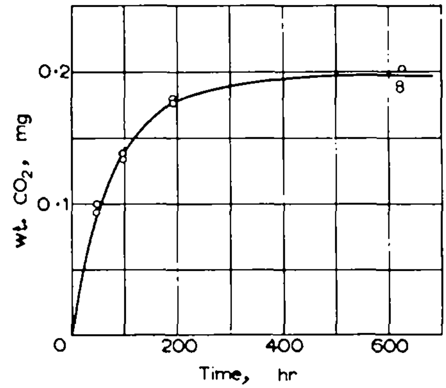

Fig. 3.

Figs. 1, 2 and 3. The variation with time of the weight of carbon dioxide formed during the decomposition of benzoyl peroxide at 60° in benzene; starting weight of peroxide = 1 mg. Initial concentrations: Fig 1, 0·05; Fig. 2, 0·50; Fig. 3, 50 g/l.

RESULTS

Benzene as solvent

The rate of production of carbon dioxide during the decomposition of benzoyl peroxide in pure benzene at 60° was measured for three concentrations of peroxide, viz., 0·05, 0·50 and 50 g/l.; the results are presented in Figs. 1, 2 and 3.

The production of carbon dioxide and the decomposition of the peroxide follow a first-order law, since straight lines were obtained by plotting:

$$\ln \frac{w_\infty - w}{w_\infty} \quad \text{against time,}$$

where w = weight of CO_2 produced after time t,
and w_∞ = weight produced at complete decomposition of the peroxide.

A typical plot is shown in Fig. 4. The results of the experiments are summarised in Table 1.

The variation with time of the weight of benzoic acid produced during the decomposition of benzoyl peroxide in solutions of initial concentration 0·50 g/l. is shown in Fig. 5. The yields of benzoic acid under these conditions were small, only about 2·5 per cent of the benzoyloxy radicals being converted to the acid. The rate of decomposition of the peroxide determined from the rate of formation of benzoic acid is in fair agreement with that determined from analyses for carbon dioxide.

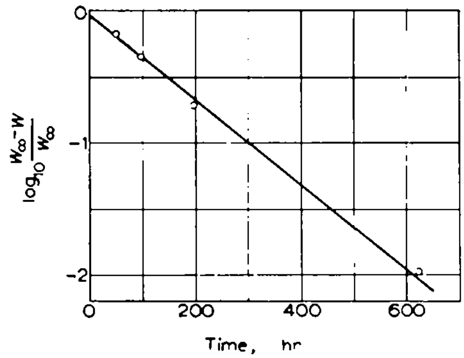

Fig. 4. A plot derived from the results shown in Fig. 2, showing that the production of carbon dioxide follows a first-order kinetic law.

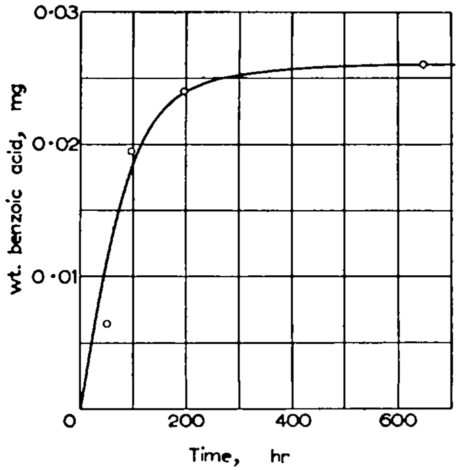

Fig. 5. The variation with time of the weight of benzoic acid formed during the decomposition of benzoyl peroxide at 60° in benzene. Initial concentration of peroxide = 0·50 g/l., initial weight of peroxide = 1 mg.

From similar experiments with peroxide at an initial concentration of 50 g/l., it was found that about 24 per cent of the benzoyloxy radicals were converted to the acid.

In an experiment with carboxyl-labelled benzoyl peroxide at a concentration of 0·5 g/l., 0·015 mg of phenyl benzoate were produced from 1 mg of peroxide after

Table 1

	Initial concentration of peroxide		
	0·05 g/l.	0·50 g/l.	50 g/l.
Weight (mg) of CO_2 from 1 mg of peroxide at complete decomposition	0·32	0·32	0·19
Percentage of benzoyloxy radicals losing CO_2	88	88	52
Velocity constant sec^{-1} for decomposition of peroxide	$2·53 \times 10^{-6}$	$2·56 \times 10^{-6}$	$4·02 \times 10^{-6}$

624 hr at 60°. Very similar yields were obtained when the concentration of the peroxide was 50 g/l.

Other solvents

When benzoyl peroxide at a concentration of 0·5 g/l. in acetic acid was decomposed at 60°, less carbon dioxide was produced than when the peroxide was decomposed in benzene under comparable conditions (see Fig. 6). The limiting yield of carbon dioxide was 0·214 mg from 1 mg of peroxide, corresponding to about 59 per cent. The decomposition followed a first-order law with a velocity constant of 4·91 × 10^{-6} sec^{-1}. Analyses for benzoic acid showed that 25 per cent of the benzoyloxy radicals were converted to that substance.

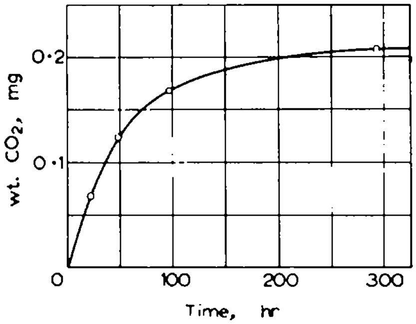

FIG. 6. The variation with time of the weight of carbon dioxide produced from benzoyl peroxide in acetic acid. Initial concentration = 0·50 g/l.

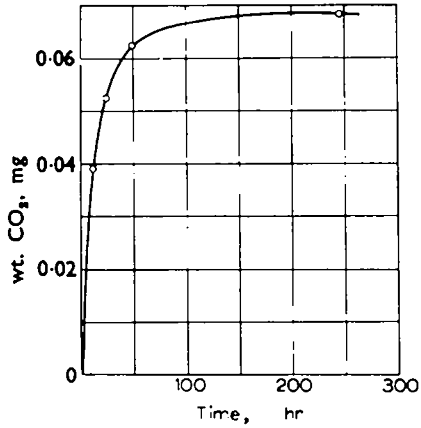

FIG. 7. The variation with time of the weight of carbon dioxide produced from benzoyl peroxide in ethanol. Initial concentration = 0·50 g/l.

It was confirmed that in ethanol benzoyl peroxide decomposes rapidly. At 60° for a solution of concentration 0·5 g/l., the velocity constant was found to be 2·15 × 10^{-5} sec^{-1}; only about 22 per cent of the benzoyloxy radicals lost carbon dioxide, while about 60 per cent were converted to benzoic acid. The results for analyses for carbon dioxide are shown in Fig. 7.

With carbon tetrachloride as solvent and peroxide at a concentration of 0·5 g/l., the velocity constant at 60° was found to be 1·39 × 10^{-6} sec^{-1}. The proportion of benzoyloxy radicals losing carbon dioxide was very close to that observed when using benzene as solvent.

Effects of added substances

The yield of carbon dioxide during the decomposition of benzoyl peroxide in benzene was reduced by the presence of diphenylpicrylhydrazyl in the reaction mixture. In a series of experiments the peroxide concentration was 0·5 g/l. and the reaction mixtures were kept at 60° for 96 hr. The results are shown in Fig. 8. The concentrations of the hydrazyl were such that in all cases it was not completely consumed.

Similar experiments were performed with thiophenol in place of the hydrazyl. This substance also was very effective in reducing the yield of carbon dioxide (see Fig. 9); at the same time the yield of benzoic acid was increased (see Fig. 10).

The variations with time of the yields of benzoic acid and carbon dioxide were not studied. It is clear however that, in addition to affecting the nature of the products, thiophenol also accelerated the decomposition of the peroxide; the evidence for this is that after only 96 hr at 60° the yield of benzoic acid approached the maximum possible value.

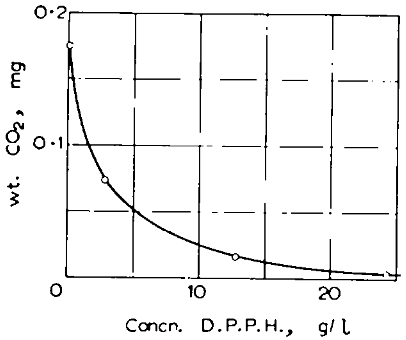

FIG. 8. The effect of diphenylpicrylhydrazyl (D.P.P.H.) upon the production of carbon dioxide during the decomposition of benzoyl peroxide in benzene at 60°. Initial concentration of peroxide = 0·50 g/l., initial weight = 1 mg, time at 60° = 96 hr.

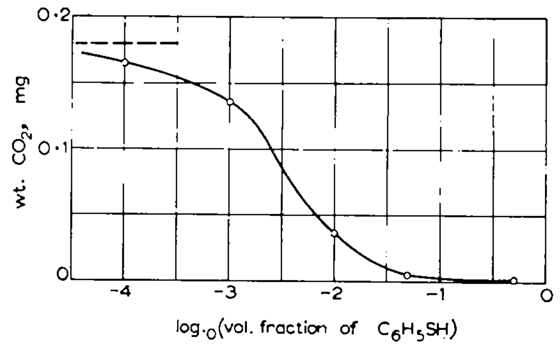

FIG. 9. The effect of thiophenol upon the production of carbon dioxide during the decomposition of benzoyl peroxide.

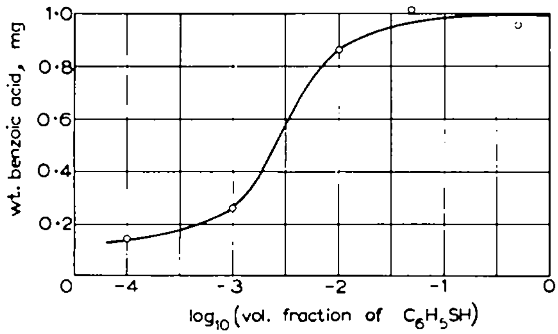

FIG. 10. The effect of thiophenol upon the production of benzoic acid during the decomposition of benzoyl peroxide.

DISCUSSION

If benzoyl peroxide is decomposed in the presence of diphenylpicrylhydrazyl or thiophenol, the yield of carbon dioxide can be reduced to zero (see Figs. 8 and 9). This shows that carbon dioxide is not produced directly during the thermal dissociation of the peroxide and that benzoyloxy radicals are the primary products of this dissociation. This is confirmed by the fact that, in the presence of sufficient thiophenol, all the benzoyl peroxide is converted to benzoic acid (see Fig. 10). In the photodissociation of the peroxide some carbon dioxide is formed during the primary process.[4]

During the decomposition of benzoyl peroxide in dilute solutions in pure benzene at 60° about 88 per cent of the benzoyloxy radicals lose carbon dioxide before they can engage in other reactions. The proportion of the radicals decomposing in this way falls as the initial concentration of peroxide is raised (see Table 1) and in solutions containing 50 g/l. only 52 per cent of the benzoyloxy radicals dissociate. Increasing the initial concentration of peroxide also causes the yield of benzoic acid to rise and the overall rate of decomposition of the peroxide to rise.

Other workers, for example, Barnett and Vaughan,[5] also have reported that the yields of carbon dioxide during the decomposition of benzoyl peroxide depend upon the concentration of the peroxide.

The dependence of the velocity constant for the decomposition of benzoyl peroxide upon the concentration of the solution is well known and has been attributed to a radical-induced decomposition.[6] Radicals produced by dissociation of the peroxide are thought to attack other molecules of peroxide and to cause them to decompose. The importance of the induced decomposition may be reduced by decreasing the concentration of the peroxide since this will increase the chance that a radical will undergo reaction before it can encounter a molecule of undissociated peroxide. In the present work with benzene as solvent, the velocity constant was hardly affected by reducing the initial concentration from 0·5 to 0·05 g/l.; this might suggest that at these concentrations the induced decomposition is practically eliminated. At a concentration of 50 g/l. however, the induced decomposition must be of considerable importance since the velocity constant is appreciably greater than at the lower concentrations.

It appears that the induced decomposition may be started by a benzoyloxy radical abstracting a hydrogen atom from a molecule of the undissociated peroxide. In this way it would be possible to account for the decrease in the proportion of the benzoyloxy radicals losing carbon dioxide and the increase in the proportion giving benzoic acid as the initial concentration of peroxide is raised. This abstraction reaction cannot be the only cause for the decrease in the yield of carbon dioxide, since, while that yield falls from 88 to 52 per cent as the concentration of peroxide is increased from 0·5 to 50 g/l., the yield of benzoic acid rises only from about 2 to 24 per cent.

When ethanol or acetic acid is used in place of benzene as solvent, the rate of decomposition of the peroxide is significantly increased; at the same time, the yield of carbon dioxide is depressed and the yield of benzoic acid is raised. These results indicate that benzoyloxy radicals abstract hydrogen atoms quite readily from ethanol or acetic acid, and that the radicals formed from the solvent can then attack molecules of undissociated peroxide.

In considering the effects of various solvents upon the production of carbon dioxide during the decomposition of benzoyl peroxide, it is necessary to measure the yields at various stages during the reaction; measuring yields at a single time

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[4] J. C. Bevington and T. D. Lewis, In preparation.

[5] B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.* **51**, 942 (1947).

[6] K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.* **68**, 1686 (1946).

only may lead to erroneous results. A solvent which causes a reduction in the proportion of benzoyloxy radicals which lose carbon dioxide, may also cause an increase in the overall rate of decomposition of the peroxide; for example, the weight of carbon dioxide produced from 1 mg of peroxide after 50 hr at 60° is greater for acetic acid as solvent than for benzene as solvent, but examination of Figs. 2 and 6 shows that actually acetic acid partially suppresses the formation of carbon dioxide.

All the experiments involving thiophenol referred to 96 hr at 60°, but it has already been pointed out that this additive must have accelerated the decomposition of the peroxide. The high yields of benzoic acid in these experiments indicate that the benzoyloxy radicals abstract hydrogen atoms very readily from molecules of thiophenol leaving the radicals C_6H_5S. There is not enough information to be certain of the subsequent reactions of these radicals but some of them must attack molecules of peroxide and so induce their decomposition; none of them can combine with benzoyloxy or phenyl radicals to give stable compounds, since in some of the experiments the yield of benzoic acid approached 100 per cent.

For benzoyl peroxide at 0·5 and 50 g/l. in benzene only very small quantities of phenyl benzoate are formed during decomposition at 60°. Lynch and Pausacker,[2] using much higher concentrations of peroxide at 78°, found also that the yields of phenyl benzoate are very low. The analyses for carbon dioxide, benzoic acid and phenyl benzoate are summarised in Table 2.

TABLE 2

Solvent	Initial concn. of peroxide (g/l.)	Benzoyloxy radicals		
		losing CO_2 (per cent)	forming C_6H_5COOH (per cent)	forming $C_6H_5COOC_6H_5$ (per cent)
Benzene	0·05	88	n.d.	n.d.
Benzene	0·50	88	2·5	1
Benzene	50	52	24	1
Acetic acid	0·50	59	25	n.d.
Ethanol	0·50	22	60	n.d.
Carbon tetrachloride	0·50	88	n.d.	n.d.

n.d. = not determined

In the dilute solutions in benzene, about 90 per cent of the benzoyloxy radicals are accounted for, but in the other solutions the percentage is lower. It is concluded that in non-reactive solvents almost all the benzoyloxy radicals dissociate to give carbon dioxide unless the concentration of the peroxide is high.

Values for the velocity constant for the decomposition of benzoyl peroxide have been determined by a variety of methods;[7] the work described here gives further values found by an alternative method. It is necessary to consider whether any of the values correspond to the primary dissociation of the peroxide molecules into

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[7] See, for example, G. A. Russell, *J. Amer. Chem. Soc.* **78**, 1044 (1956).

benzoyloxy radicals. The velocity constant for the decomposition of the peroxide may include a contribution from the induced decomposition, and so the lowest value observed for this velocity constant is the one most likely to correspond to the primary dissociation. High rates are observed when the concentration of peroxide in benzene is fairly high, when ethanol or acetic acid is used as solvent and when thiophenol is present in the solution; clearly under these conditions the induced decomposition is of importance It is very significant that the rate in carbon tetrachloride is considerably less than that in benzene, even when the concentration of peroxide is low; the velocity constant found for decomposition in carbon tetrachloride and benzene, in both cases for peroxide at 0·5 g/l., are $1·39 \times 10^{-6}$ sec^{-1} and $2·56 \times 10^{-6}$ sec^{-1}, respectively.

One of the methods frequently employed for suppressing the induced decomposition of benzoyl peroxide is to perform the decomposition in the presence of radical scavengers; polymerisable monomers can be used for this purpose and among those which have been used are styrene,[1] dichlorostyrene[8] and methyl methacrylate.[9] It is possible that growing polymer radicals might give rise to the induced decomposition however, and this type of objection can be raised against any scavenger which reacts with radicals to give new radicals. In the case of styrene and methyl methacrylate, rates of initiation of polymerisation were measured by a tracer technique and the velocity constant for the decomposition of benzoyl peroxide at 60° was found to be $1·5 \times 10^{-6}$ sec^{-1} (with styrene) and $1·6 \times 10^{-6}$ sec^{-1} (with methyl methacrylate). If polystyrene and poly(methyl methacrylate) radicals are capable of inducing the decomposition of benzoyl peroxide, it would be very unlikely that they would be equally effective, and it appears that these values for the velocity constant may correspond to the primary dissociation.

The most satisfactory type of scavenger is one which reacts with radicals to give inert products incapable of further reaction with free radicals; a stabilised radical might act as a scavenger of this type. Bawn and Mellish[10] measured the rate of decomposition of benzoyl peroxide by following its reaction with the coloured radical diphenylpicrylhydrazyl. There was, however, a significant variation of velocity constant with solvent; this variation would not have been observed if the scavenger had behaved ideally. Another objection to the use of the hydrazyl is that products formed by its interaction with radicals are themselves reactive; this is shown by the fact that these products are retarders for radical polymerisations.[11]

Other workers have noticed that benzoyl peroxide decomposes rather slowly in highly halogenated solvents.[6] It is possible that these solvents favour a cage effect, so that radicals readily recombine with their original partners; it is very doubtful whether such a large difference between the rates in carbon tetrachloride and benzene could be accounted for thus, but a cage effect might be responsible for the difference between the rate observed in carbon tetrachloride and those in styrene and methyl methacrylate. The difference between the results obtained with two monomers might be accounted for by errors in the determinations of the absolute rates of polymerisation. It seems to be an inevitable conclusion that even in the very dilute solutions of

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[8] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Amer. Chem. Soc.* **72**, 5426 (1950).

[9] J. C. Bevington, *Trans. Faraday Soc.* **53**, 997 (1957).

[10] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.* **47**, 1216 (1951).

[11] J. C. Bevington, *J. Chem. Soc.* 1127 (1956).

the peroxide in benzene, there still remains a contribution from an induced decomposition; this may be initiated by the attack of phenyl radicals upon molecules of peroxide.

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