572. *Kinetics of the Reaction between Benzoyl Peroxide and Phenols.*

By J. J. Batten and M. F. R. Mulcahy.

The reaction between benzoyl peroxide and a phenol in an inert solvent is not a chain reaction but occurs mainly by direct interaction between the phenol and peroxide molecules. It is suggested that the initial step is:

$$\mathrm{ArOH + Ph{\cdot}CO{\cdot}O{-}O{\cdot}COPh \longrightarrow ArO{\cdot} + Ph{\cdot}CO{\cdot}OH + {\cdot}O{\cdot}COPh}$$

and that this is probably preceded by the formation of a hydrogen bond between the phenol and the carbonyl oxygen atom.

In a "reactive" solvent (*e.g.*, dioxan) this reaction is superimposed on the inhibiting effect of the phenol on the solvent-induced chain decomposition of the peroxide.

The decomposition of benzoyl peroxide in solution occurs primarily by unimolecular fission of the O–O bond:

$$\mathrm{Ph{\cdot}CO{\cdot}O{-}O{\cdot}COPh \longrightarrow 2Ph{\cdot}CO{\cdot}O{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In a solvent (SH) containing a weak C–H bond, both the kinetic behaviour [1] and the nature of the products [2] show that the benzoate radicals initiate a chain reaction involving more peroxide molecules:

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot} + SH \longrightarrow Ph{\cdot}CO{\cdot}OH + S{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{S{\cdot} + Ph{\cdot}CO{\cdot}O{-}O{\cdot}COPh \longrightarrow Products + Ph{\cdot}CO{\cdot}O{\cdot}} \quad . \; . \; . \; . \quad (3)$$

The rate of disappearance of peroxide from such a solvent may be many times greater than from an "unreactive" solvent such as benzene or chloroform, where the chain reaction occurs to only a minor extent. The peroxide disappears very rapidly from solution in a liquid phenol, and previous authors have assumed that this takes place by a similar chain reaction,[3–5] the radical S· being identified with the ArO· radical.[6] This receives some

---

[1] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

[2] Cass, *ibid.*, 1947, **69**, 500.

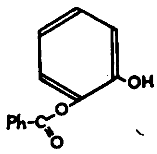
[3] Bartlett and Nozaki, *ibid.*, p. 2299.

[4] Tipper, *J.*, 1952, 2966.

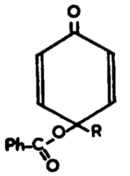
[5] Batten and Mulcahy, *Nature*, 1953, **172**, 72.

[6] Cosgrove and Waters, *J.*, 1951, 388.

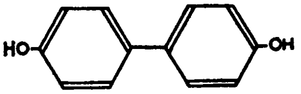
support from the well-known susceptibility of the phenolic O–H bond to free-radical attack. Nevertheless, a simple explanation in terms of this mechanism is precluded by the fact that the decomposition in a reactive solvent, *e.g.*, *cyclo*hexane or dioxan, is retarded by small amounts of phenols.[1,7] On increase of the phenol concentration, however, the rate of disappearance of peroxide passes through a minimum and the retardation is replaced by an acceleration.[5] This increases roughly in proportion to the phenol concentration and evidently reaches its limit in the pure phenol. Any mechanism which purports to explain the high rates observed in the liquid phenol or at high phenol concentrations in reactive solvents must therefore also take into account the retarding effect at low concentrations. It is with this problem that this and the following paper are concerned. This paper describes a study of the effect of quinol and *p*-methoxyphenol on the rate of disappearance of the peroxide from various solvents, these phenols being chosen because they manifest both the retarding and the accelerating effects to a convenient degree. The influence of the structure of the phenol on the magnitude of these effects is discussed in the following paper.



(I)



(II)



(III)

The products of the reaction of benzoyl peroxide with various substituted phenols in chloroform solution at 61° have been examined by Cosgrove and Waters.[6,8] These are for the most part benzoic acid and, depending on the positions of the substituents, benzoate derivatives of types (I) or (II) or diphenols (III) and their quinonoid oxidation products. Analogous products are obtained with acetyl peroxide.[9]

EXPERIMENTAL

Procedure.—The disappearance of benzoyl peroxide from solution was followed in the absence of air by analysis for residual peroxide at successive intervals. Solutions (12 ml.) of peroxide and phenol of appropriate concentration were prepared in Pyrex ampoules, degassed by repeated freezing and melting *in vacuo*, sealed off, and immersed in an oil-thermostat. When the rate was appreciable at room temperature two-legged ampoules were used; the solutions of peroxide and phenol were brought separately to the temperature of the thermostat and then mixed. At the appropriate time an ampoule was cooled rapidly by shaking in cold water or in an ice–salt bath, and the peroxide content determined iodometrically. Light was excluded in all operations. The thermostat temperature was measured by a calibrated thermometer and remained constant within ±0·05°.

The general kinetic behaviour was first explored by studying the effect of the phenol concentration on the amount of peroxide remaining after a specified time. Since, however, the products were likely to influence the rate, the final kinetic analysis was based on measurements of the initial rate. Each measurement was derived from four determinations of the peroxide concentration made before the first 12% (at the most) of the peroxide had reacted. The experiments with benzene solutions at 30° were carried out with the two-legged ampoules. In those with dioxan, however, the peroxide and phenol were mixed at room temperature. Experiments with thermocouples showed that in this case 3 min. were required for the solution to reach within 0·5° of the thermostat temperature at 80°. Under the most unfavourable conditions the heat of reaction produced no perceptible rise in the temperature of the solution. Plots of the peroxide content against time were linear within the experimental error, and passed through the origin when the two-legged ampoules were used. The reproducibility of the individual determinations of the peroxide concentration was within ±0·5% of the original concentration. No induction periods were observed.

[7] Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

[8] Cosgrove and Waters, *J.*, 1949, 3189.

[9] Wessely and Schinzel, *Monatsh.*, 1953, **84**, 425, 969.

Analytical Methods.—The method of analysis for peroxide was based on that of Nozaki,[10] in which iodine is liberated from potassium iodide in acetic anhydride solution. The rate of liberation of iodine was found to be influenced by the presence of the solvent in which the decomposition had been carried out, and especially by phenols. Consequently, the conditions for quantitative liberation were established in control experiments.[11] With quinol and some other phenols the presence of quinones in the products limits the applicability of direct iodometric determination of the residual peroxide. For this reason the study of the behaviour in a reactive solvent was made with dioxan. The peroxide could then be separated from the products by precipitation with water containing a trace of acetic acid. The absence of colour from the precipitate and a negative test with potassium iodide on the washings were taken to indicate the absence of quinones. Occasionally a second or third re-precipitation was required. No appreciable loss of peroxide occurred during this procedure. The technique also eliminated catalysed autoxidation of the dioxan during the period of iodine liberation which otherwise led to high results. The method is inapplicable with solvents immiscible with water. Here the choice of phenols was restricted to those which gave no strong indication of quinone formation in dioxan. This condition was particularly well satisfied by *p*-methoxyphenol.

The reaction with quinol in dioxan produces *p*-benzoquinone as the major product. In these and in some other experiments in which *p*-benzoquinone was added to the reaction mixture the quinone was determined in the filtrate by direct titration with thiosulphate.[12]

Materials.—Commercial benzoyl peroxide was precipitated from chloroform solution by methanol and dried *in vacuo*; before use it was recrystallised twice from dry, peroxide-free ether and dried *in vacuo* in the dark. This material liberated 100·0—100·2% of the theoretical amount of iodine. Quinol was twice recrystallised from distilled water containing a trace of hydrochloric acid, and dried *in vacuo* (m. p. 172·0—172·5°). *p*-Methoxyphenol and phenol were recrystallised three times from *cyclo*hexane and dried *in vacuo* (m. p. 55·5—56·0° and 40·6—40·9° respectively). *p*-Benzoquinone was sublimed and recrystallised from water (m. p. 113·5—114·5°). Dioxan, purified by the method of Swain *et al.*,[7] was fractionally recrystallised twice and stored over sodium (b. p. 101·4°; n_D^{20} 1·4224, Abbé). Tests for peroxide were always negative. "AnalaR" benzene was purified by treatment with sulphuric acid, fractional recrystallisation, and distillation, and stored over sodium (b. p. 80·2°; n_D^{20} 1·5010, Abbé). Acetophenone was purified by fractional crystallisation and distillation[13] (b. p. 201°; n_D^{20} 1·5341, Abbé). "AnalaR" chloroform was purified by Weissberger and Proskauer's method.[14] All solvents were stored in darkness at 0°.

RESULTS

The effect of a phenol on the rate of disappearance of benzoyl peroxide from a reactive solvent is illustrated by comparison of the effect of quinol (Fig. 1*a*) in dioxan with that of *p*-benzoquinone (Fig. 1*b*) under the same conditions. Each of the curves in Figs. 1*a* and 1*b* gives the amount of peroxide which reacted in a fixed period as a function of the initial quinol or quinone concentration. (In the experiments referred to in these and in subsequent figures, unless otherwise indicated, the initial peroxide concentration was 50 mM and the temperature 80·65°.) Quinone in sufficient concentration reduces the amount of peroxide reacting to a limiting value which is unaffected by further increase in concentration. This is similar to the effect of vinyl monomers and the other retarders studied by previous investigators.[7, 15] The limiting rate is that of the primary "spontaneous" fission of the peroxide molecules [reaction (1)].* With quinol, however, no limiting rate is observed. Small initial concentrations retard the reaction, but at higher concentrations this is counteracted by an accelerating effect. Similar behaviour is exhibited by other phenols in *cyclo*hexane solution[5] (cf. also ref. 16). There is little doubt that it is characteristic of phenols in general. Thus the reaction of benzoyl peroxide with phenols is more complicated kinetically than its reaction with other retarders such as quinone, vinyl monomers, and polynuclear hydrocarbons.[17]

---

* The present experiments gave a unimolecular rate constant of $2{\cdot}56 \times 10^{-3}$ min.$^{-1}$ in good agreement with the value of $2{\cdot}52 \times 10^{-3}$ min.$^{-1}$ obtained by Swain *et al.*[7] at 80°.

[10] Nozaki, *Ind. Eng. Chem. Anal.*, 1946, **18**, 583.
[11] Batten, Thesis, Melbourne, 1955.
[12] Rzymkowski, *Z. Elektrochem.*, 1925, **31**, 371.
[13] Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, 1950.
[14] Weissberger and Proskauer, "Organic Solvents," Oxford, 1935.
[15] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.
[16] Batten, following paper.
[17] Batten, unpublished.

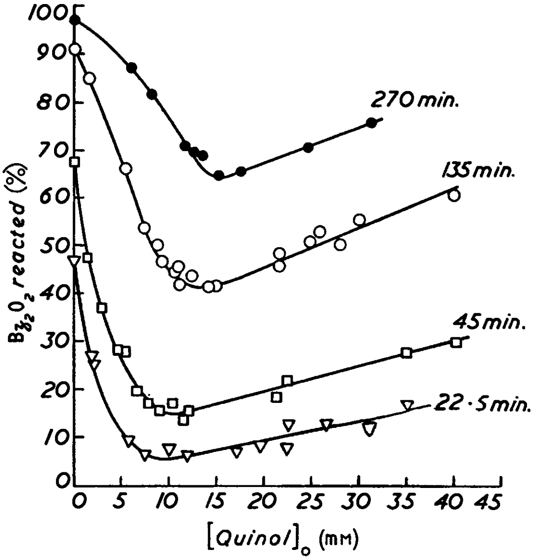


FIG. 1*a*. *Effect of initial quinol concentration on total amount of benzoyl peroxide which has reacted in dioxan in various times.* Initial benzoyl peroxide concentration ($[Bz_2O_2]_0$) = 50 mM; T = 80·65°.

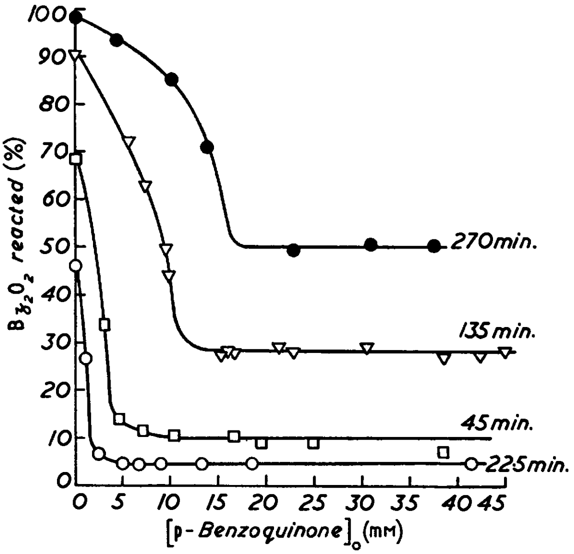


FIG. 1*b*. *Effect of initial* p*-benzoquinone concentration on total amount of benzoyl peroxide reacting in dioxan in various times.*

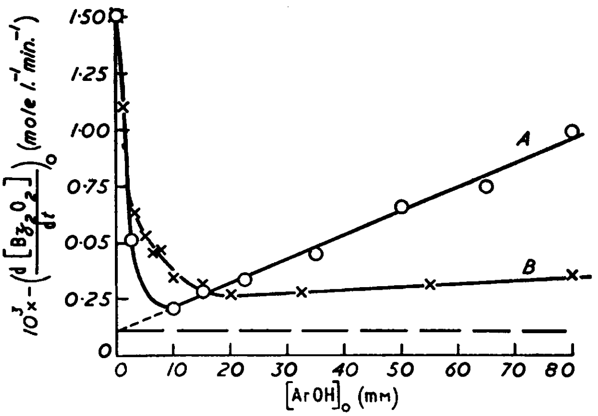


FIG. 2. *Variation of initial rate of disappearance of benzoyl peroxide from dioxan with initial concentrations of* (*A*) *quinol and* (*B*) p*-methoxyphenol.*

The horizontal broken line refers to the rate corresponding to complete suppression (by *p*-benzoquinone) of the solvent-induced chain decomposition.

The influence of quinol on the initial rate in dioxan is shown by curve *A* of Fig. 2. It will be seen that the accelerating effect which replaces the retardation observed at lower concentrations increases linearly with the concentration. Furthermore, the straight line when extrapolated back to zero concentration meets the ordinate at the rate of the "spontaneous" decomposition. At concentrations corresponding to the linear part of the curve, analysis showed that in the early stages of reaction one quinone molecule is formed for every peroxide molecule which disappears. It is therefore probable that the quinol is converted quantitatively into *p*-benzoquinone. Since, however, the main products from monohydric phenols are more often similar to (I) and (II), *i.e.*, contain a fragment of the peroxide, this raises the possibility that the kinetic behaviour of quinol may not be typical. Further experiments were therefore carried out with *p*-methoxyphenol which gives a product similar to (II).[8]

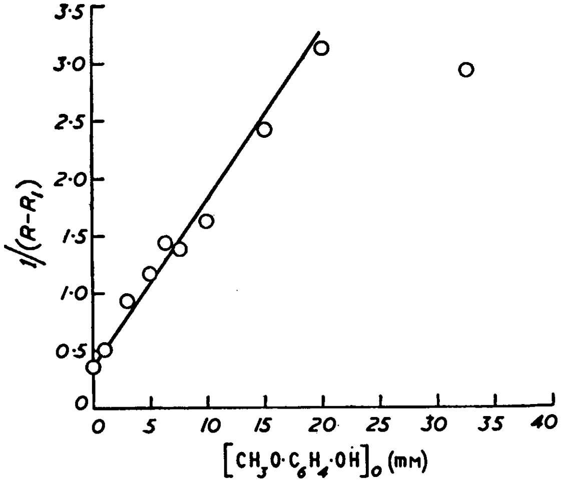


FIG. 3. *Variation of* $1/(R - R_1)$ *with initial* p-*methoxyphenol concentration in dioxan.*

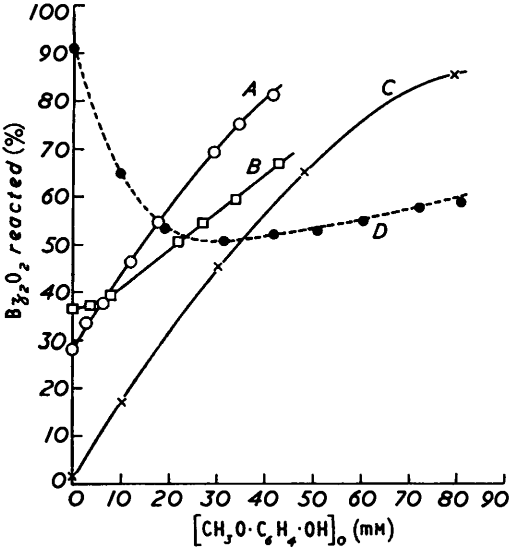


FIG. 4. *Effect of initial* p-*methoxyphenol concentration on amount of benzoyl peroxide reacting in* 135 *min. in* (*A*) *benzene,* (*B*) *acetophenone,* (*C*) *chloroform* (*T* = 60·3°), *and* (*D*) *dioxan.*

The variation of the initial rate with *p*-methoxyphenol concentration is shown by curve *B* in Fig. 2. The behaviour is similar to that of quinol but the accelerating and retarding effects are less sharply delineated. Nevertheless, at initial *p*-methoxyphenol concentrations less than about 15 mM the accelerating effect can probably be neglected in comparison with the retarding effect. If in this region the phenol behaves as a retarder of the usual type, the following approximate relationship would then be expected to hold :

$$R - R_1 \approx A/(1 + B[\mathrm{ArOH}]_0) \quad \ldots\ldots\ldots \quad \text{(i)}$$

where R is the total rate, R_1 the rate of reaction (1), and A and B are constants; $1/(R - R_1)$ would thus be approximately linearly related to $[\mathrm{ArOH}]_0$. That this is the case is shown by Fig. 3.

The increase in rate at higher concentrations (Fig. 2) appears to be directly proportional to the phenol concentration as in the case of quinol, but it is not clear to what extent the retarding effect is still influencing the kinetics. However, it should be possible to isolate the accelerating effect from the retarding effect by studying the kinetics in a solvent where the solvent-induced chain decomposition of the peroxide is small. The effect of the phenol concentration on the rate in three such solvents is shown in a semiquantitative fashion by curves A, B, and C in Fig. 4, and may be compared with its effect in dioxan in similar circumstances (curve D). In the " unreactive " solvents the accelerating effect is predominant over the whole range of concentration. Similar behaviour can be observed in dioxan if sufficient *p*-benzoquinone (or picric acid)[11] is present to inhibit the induced decomposition completely. This is shown for two quinone concentrations (cf. Fig. 1*b*) in Fig. 5. (It is noteworthy that in both cases when the phenol was in sufficient excess the total amount of quinone added originally was found in the products.) However, the addition of quinone complicates the analysis, and the kinetics of the accelerating effect are therefore best investigated in an unreactive solvent. Of these, benzene was found the most suitable.

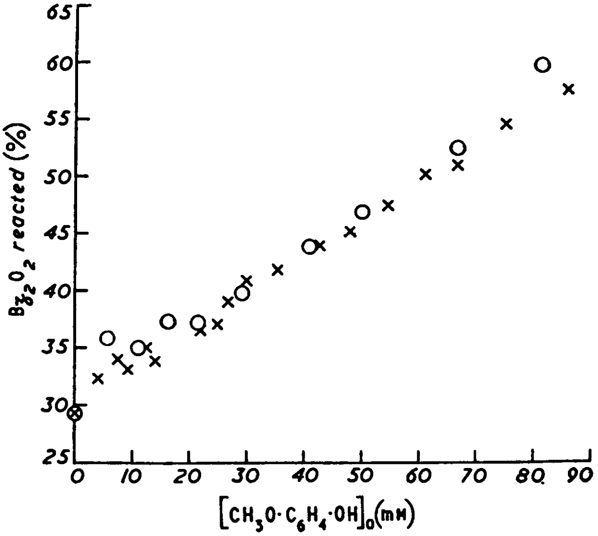


FIG. 5. *Effect of initial* p-*methoxyphenol concentration on amount of benzoyl peroxide reacting in* 135 *min. in dioxan in the presence of* (×) 16 *and* (○) 50 mM *of* p-*benzoquinone.*

The effects of the phenol and peroxide concentrations on the initial rate in benzene are shown in Figs. 6 and 7. The rate increases linearly with the concentrations of both reagents over the greater part of the concentration range. Deviations (which are outside the experimental error) occur at high peroxide and low phenol concentrations, but it is clear that in the range studied the rate is given approximately by

$$-\mathrm{d}[\mathrm{Bz_2O_2}]/\mathrm{d}t = k[\mathrm{Bz_2O_2}][\mathrm{ArOH}] \quad \ldots\ldots\ldots \quad \text{(ii)}$$

This is in agreement with results obtained by previous investigators with the reaction in liquid phenols : Bartlett and Nozaki[3] and Tipper[4] found first-order kinetics with respect to the peroxide concentration, and Tipper observed that the (pseudo-)unimolecular rate constant decreased approximately in proportion as the phenol was diluted with water. In the present experiments at 30° when $[\mathrm{Bz_2O_2}]/[\mathrm{ArOH}] > \sim 1$, the rate is more dependent on [ArOH] and less dependent on $[\mathrm{Bz_2O_2}]$ than equation (ii) would indicate. On the other hand, Fig. 6 shows that it deviates less from a linear dependence on [ArOH] as the temperature is increased. It should be noted that the rate with phenol absent is far too small for the deviation to be accounted for by inhibition of solvent-induced decomposition by the phenol. At 30·2° the value of k obtained from the slope of the linear part of the curve in Fig. 6 is $3{\cdot}8 \times 10^{-2}$ l. mole^{-1} min.$^{-1}$, in fair agreement with the value $2{\cdot}9 \times 10^{-2}$ l. mole^{-1} min.$^{-1}$ derived from Fig. 7. The activation energy obtained from the slopes of the curves in Fig. 6, corrected for the change in peroxide concentration due to thermal expansion of the solvent, is 11·0 kcal. mole^{-1}.

FIG. 6. *Variation of initial rate in benzene with initial concentration of* p-*methoxyphenol at three temperatures.*

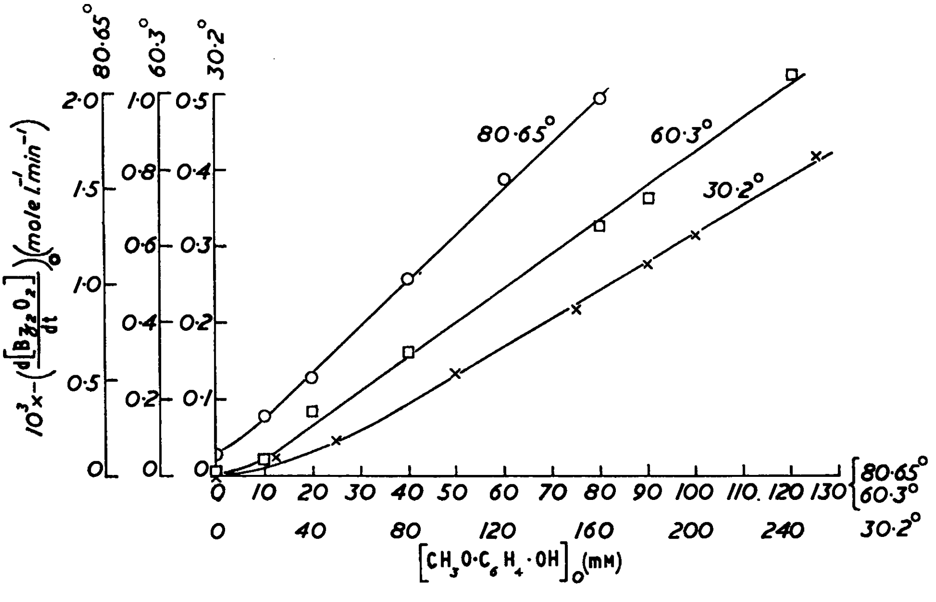
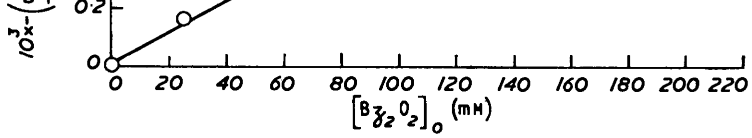


FIG. 7. *Variation of initial rate in benzene with initial concentration of benzoyl peroxide.* Initial *p*-methoxyphenol concentration = 200 mM; T = 30·2°.



Tests for a Chain Reaction (in an Unreactive Solvent).—The reaction in benzene is clearly identical with that which occurs in liquid phenols and is predominant at high phenol concentrations in reactive solvents. However, the dependence of the rate on the first power of both $[Bz_2O_2]$ and [ArOH] conflicts with the view that it is a chain reaction similar to other solvent-induced decompositions, *i.e.*, that it proceeds by reactions (1)—(3). The manner in which the rate of such a reaction varies with the reagent concentrations depends on the particular radicals which participate in chain termination, but no plausible termination reaction leads to equation (ii). This can be remedied by postulating that initiation occurs mainly by a bimolecular reaction between the peroxide and the phenol rather than by reaction (1), but then it is difficult to account for the inhibiting effect in reactive solvents. An alternative view is that the reaction in unreactive solvents and in the pure phenol is simply a bimolecular non-chain reaction; and that in the reactive solvents this occurs simultaneously with and independently of the inhibiting effect of the phenol on the solvent-induced decomposition.

The following experiments were carried out with the object of deciding between these views. If the reaction is a chain reaction it should be susceptible to inhibition. However, the results given in Fig. 5 show that the rate is not reduced by *p*-benzoquinone, and Tables 1, 2, and 3 show similar results with oxygen, anthracene, styrene, and picric acid.* These substances all inhibit the induced decomposition in non-phenolic solvents.[16,17] Table 3 refers to experiments carried out in liquid phenol. Tipper [4] and Bartlett and Nozaki [8] have shown that oxygen has no effect on the rate in liquid phenols. These results taken together provide strong evidence against a chain reaction but are not completely conclusive since the chain carriers could conceivably propagate the chain at a greater rate than they react with any of the inhibitors chosen. However, if the peroxide reacts mainly by a chain reaction, an increase in the rate of initiation will produce a large effect on the overall rate. Thus, if the rate of primary production of radicals by reaction (1) is increased by irradiation with ultraviolet light, the consequent increment in the total rate of disappearance of peroxide will be at least several times greater. On the other hand, if chains are not involved no increase in the total rate will be observed other than that due directly to the photolysis of the peroxide.

TABLE 1. *Effect of anthracene and styrene on the rate of reaction between* p-*methoxyphenol and benzoyl peroxide in benzene solution.* $[\mathrm{Bz_2O_2}]_0 = 50$ mM; $T = 80{\cdot}65°$.

$[\mathrm{MeO{\cdot}C_6H_4{\cdot}OH}]_0$ (mM)	[Anthracene]$_0$ (mM)	[Styrene]$_0$ (mM)	Bz$_2$O$_2$ reacting in 135 min. (%)	$[\mathrm{MeO{\cdot}C_6H_4{\cdot}OH}]_0$ (mM)	[Anthracene]$_0$ (mM)	[Styrene]$_0$ (mM)	Bz$_2$O$_2$ reacting in 135 min. (%)
0	0	0	28·0	41·2	0	—	82·0
					100	—	82·5
0	100	—	28·4	43·8	—	—	84·0
0	—	36·4	27·0		—	36·4	84·2
0	—	72·8	26·9		—	72·8	84·0
21·6	0	—	60·5				
	100	—	61·2				

TABLE 2. *Effect of oxygen on the initial rate of reaction between* p-*methoxyphenol and benzoyl peroxide in benzene.* $[\mathrm{Bz_2O_2}]_0 = 50$ mM; $T = 60{\cdot}3°$.

$[\mathrm{MeO{\cdot}C_6H_4{\cdot}OH}]_0$ (mM)		0	20	120
Initial rate (mM min.$^{-1}$)	*ca.* 6 ml. of O$_2$ (N.T.P.) *	0·0087 †	0·19	1·14
	in vacuo	0·0077	0·17	1·05

* This refers to the volume of oxygen above the solution at the beginning of the experiment; the solutions were shaken from time to time during the experiments.

† The accuracy of the iodometric analysis is impaired when the solution is saturated with oxygen.

TABLE 3. *Effect of* p-*benzoquinone, picric acid, and anthracene on the reaction between phenol and benzoyl peroxide in liquid phenol.* $[\mathrm{Bz_2O_2}]_0 = 50$ mM; $T = 80{\cdot}65°$.

Inhibitor	[Inhibitor]$_0$ (mM)	Bz$_2$O$_2$ reacting in 22·5 min. (%)	Inhibitor	[Inhibitor]$_0$ (mM)	Bz$_2$O$_2$ reacting in 22·5 min. (%)
—	—	81·8	Picric acid	233	98·5
p-Benzoquinone	202	80·4	Anthracene	217	98·2

Oxygen-free solutions of peroxide in chloroform were therefore exposed to the light of a low-pressure mercury arc with and without *p*-methoxyphenol present. The lamp emitted 99% of its radiation as the 2537 Å line, at which wavelength the extinction coefficient of benzoyl peroxide [18] is at least 10 times that of *p*-methoxyphenol.[19] To reduce absorption by the phenol still further, the experiments were carried out with an excess of peroxide. The solutions were irradiated at room temperature in a quartz vessel provided with a plane window, care being

---

* It was also found that the simultaneous effect of two phenols on the rate in benzene is approximately equal to the sum of their separate effects.

[18] Breitenbach and Derkosch, *Monatsh.*, 1950, **81**, 530.

[19] Waljaschko, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 226.

taken to ensure that the same quantity of light entered the vessel in different experiments. Columns 5 and 6 of Table 4 show the amount of peroxide which reacted after 30 minutes' irradiation and after the same time in the dark, respectively. It will be seen that when allowance is made for the dark reaction the amount of peroxide which disappeared as the result of the light absorption was not affected, within the experimental error, by the presence of the phenol. This indicates clearly that the phenol does not participate in a chain reaction involving the peroxide.

TABLE 4. *Influence of ultraviolet light on the reaction between benzoyl peroxide and phenols at room temperature.*

				Bz_2O_2 reacted after 30 min. (%)		
Solvent	Phenol	$[Bz_2O_2]_0$ (mM)	$[\text{Phenol}]_0$ (mM)	Light reaction (L)	Dark reaction (D)	L − D
Chloroform	*p*-Methoxyphenol	200	0	$18{\cdot}_4$	$1{\cdot}_4$	$17{\cdot}_0$
			25·3	$14{\cdot}_8$	$0{\cdot}_0$	$14{\cdot}_8$
			50	$21{\cdot}_1$	$3{\cdot}_9$	$17{\cdot}_2$
			100	$22{\cdot}_5$	$7{\cdot}_6$	$14{\cdot}_9$
		400	0	$11{\cdot}_8$	$0{\cdot}_8$	$11{\cdot}_0$
			50	$15{\cdot}_4$	$4{\cdot}_9$	$10{\cdot}_5$
			100	$20{\cdot}_7$	$8{\cdot}_4$	$12{\cdot}_3$
Dioxan	*p*-Methoxyphenol	100	0	$39{\cdot}_4$	$0{\cdot}_6$	$38{\cdot}_8$
			25	$30{\cdot}_6$	$0{\cdot}_7$	$29{\cdot}_9$
			50	$26{\cdot}_9$	$0{\cdot}_0$	$26{\cdot}_9$
			75	$28{\cdot}_0$	$0{\cdot}_0$	$28{\cdot}_0$
	Mesitol	100	25	$33{\cdot}_2$	$2{\cdot}_6$	$30{\cdot}_6$
			50	$31{\cdot}_5$	$2{\cdot}_8$	$28{\cdot}_7$
			75	$31{\cdot}_9$	$4{\cdot}_3$	$27{\cdot}_6$
*cyclo*Hexane	*p*-Methoxyphenol	20	0	$75{\cdot}_0$	$9{\cdot}_0$	$66{\cdot}_0$
			5	$68{\cdot}_3$	$10{\cdot}_7$	$57{\cdot}_6$
			10	$58{\cdot}_9$	$10{\cdot}_1$	$48{\cdot}_8$
			15	$58{\cdot}_7$	$12{\cdot}_0$	$46{\cdot}_7$

The results of some photochemical experiments carried out in dioxan and *cyclo*hexane are also shown in Table 4. Here the light initiates solvent-induced decomposition and the photo-rate in the absence of phenol is greater than the corresponding rate in chloroform. The phenol has now two effects: it suppresses the induced decomposition to a limiting rate, *i.e.*, to that of the primary photolysis [reaction (1)], and at the same time reacts directly with the peroxide. The resultant effect is completely analogous to that found in the absence of light (cf. Fig. 1*a*), except that here the direct reaction between phenol and peroxide is relatively slow because of the lower temperature.

DISCUSSION

The kinetic properties, the insensitivity of the rate to inhibitors, and the result of the photochemical experiments establish conclusively that the reaction in an unreactive solvent is not a chain reaction. Furthermore, the evidence leaves little doubt that the same reaction occurs in the pure phenol. Phenols, therefore, cannot be regarded as "reactive" solvents in the same sense as ethers, alcohols, and aliphatic hydrocarbons which undoubtedly involve the peroxide in a chain reaction.

When a phenol is added to a solution of peroxide in an ether, alcohol, or aliphatic hydrocarbon, the chain reaction is suppressed by substitution of the reaction

$$\text{Ph·CO·O·} + \text{ArOH} \longrightarrow \text{Ph·CO}_2\text{H} + \text{ArO·} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for reaction (2), or the reaction

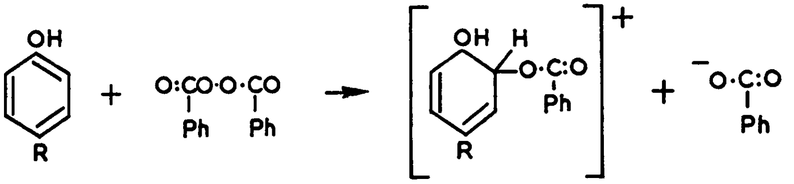
$$\text{S·} + \text{ArOH} \longrightarrow \text{SH} + \text{ArO·}$$

for reaction (3), the ArO· radical evidently being much less active in attacking the peroxide than the S· radical (cf. Fig. 3 and Batten [16]). At the same time the direct reaction between phenol and peroxide also occurs. Since with increasing phenol concentration the rate of the solvent-induced reaction is reduced to a limit but that of the direct reaction increases continuously, the inhibiting effect at low concentration will eventually be more than counterbalanced by the direct reaction. This then is the explanation of the curves in

Figs. 1*a* and 2. A previous tentative explanation [5] based on the assumption that the reaction at high phenol concentrations was a chain reaction is now superseded.

In an inert solvent the situation is no longer complicated by the reaction of the peroxide with solvent radicals, and two distinct modes of reaction with the phenol can be more easily distinguished. First, there is the direct reaction, and secondly, there can be little doubt that the Ph·CO·O· radicals from the unimolecular fission of the peroxide will attack phenol molecules to give benzoic acid [reaction (4)] together with products resulting from combination of the ArO· radicals with each other and/or with Ph·CO·O· radicals. Under the present conditions with comparable concentrations of phenol and peroxide the direct reaction is the faster. Curve *C* in Fig. 4 shows that the direct reaction between equimolecular concentrations of *p*-methoxyphenol and peroxide in chloroform at 60° is about 50 times faster than the unimolecular decomposition. This leaves no doubt that the products—benzoic acid and 2-benzoyloxy-5-methoxyphenol (type I)—obtained in high yield by Cosgrove and Waters [8] by refluxing (considerably higher) equimolecular concentrations in chloroform (61°) are products of the direct reaction. The present experiments show that with quinol the direct reaction produces benzoquinone. It is noteworthy that these products are what could very reasonably be expected from the sequence of reactions just envisaged as following on the production of Ph·CO·O· radicals by the unimolecular decomposition; and indeed, this sequence was assumed originally by Cosgrove and Waters to account for the composition of the products. This suggests, though it does not prove, that the direct reaction itself produces Ph·CO·O· radicals.

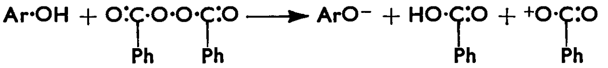
We may now consider the nature of the direct interaction between phenol and peroxide. One possibility * is that a nuclear electrophilic substitution analogous to halogenation occurs :



. (5)

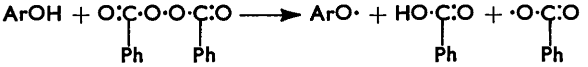
With a *p*-substituted phenol this would lead to a product of type (I), but it must be ruled out on two grounds. First, reaction (5) would be faster in a polar than in a non-polar solvent [19a] but the actual reaction is considerably slower in dioxan than in benzene or chloroform. Secondly, the formation of benzoquinone from quinol indicates that with quinol a phenolic hydrogen atom is involved in the reaction and the steric effects discussed in the following paper show this also to be the case with other phenols.

The most obvious way in which the phenolic hydrogen can react with the peroxide is by attaching itself to the carbonyl oxygen atom. This could conceivably occur either heterolytically or homolytically, *viz.* :



$$\mathrm{Ar{\cdot}OH} + \mathrm{O{:}\underset{Ph}{C}{\cdot}O{\cdot}O{\cdot}\underset{Ph}{C}{:}O} \longrightarrow \mathrm{ArO^-} + \mathrm{HO{\cdot}\underset{Ph}{C}{:}O} + \mathrm{{}^+O{\cdot}\underset{Ph}{C}{:}O} \quad . \ . \ . \ . \ . \quad (6)$$

or



$$\mathrm{ArOH} + \mathrm{O{:}\underset{Ph}{C}{\cdot}O{\cdot}O{\cdot}\underset{Ph}{C}{:}O} \longrightarrow \mathrm{ArO{\cdot}} + \mathrm{HO{\cdot}\underset{Ph}{C}{:}O} + \mathrm{{\cdot}O{\cdot}\underset{Ph}{C}{:}O} \quad . \ . \ . \ . \ . \quad (7)$$

Reaction (6) amounts to acid-catalysed decomposition of the peroxide by the phenol, and consequently is to be rejected since Bartlett and Leffler [19b] have shown that the decomposition is only slightly susceptible to acid catalysis. Indeed, the effects of benzoic,[11] trichloroacetic,[19b] and probably even sulphuric acid [19b] on the rate are very much smaller

---

* Suggested by a Referee.

[19a] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 347.

[19b] Bartlett and Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 3030.

than those of *p*-methoxyphenol and quinol which are, of course, very much weaker acids. Furthermore, no relation can be discerned between the rates of reaction of different phenols (cf. following paper) and their ionisation constants. It appears therefore that we are left with the homolytic reaction (7). This reaction is in accord with the second-order kinetics and does not conflict with the effect of the solvent or the nature of the products. The Ph·CO·O· and (mesomeric) ArO· radicals will be formed within the same " cage " of solvent molecules and combination between them will lead to products of types (I) and (II). In other circumstances the Ph·CO·O· radical may attack another phenol molecule to produce a second ArO· radical [reaction (4)] and mutual combination between ArO· radicals will give rise to diphenols (III). Benzoquinone is presumably produced from quinol by abstraction of the second phenolic hydrogen from the $HO{\cdot}C_6H_4{\cdot}O{\cdot}$ radical by the Ph·CO·O· radical or by disproportionation between two $HO{\cdot}C_6H_4{\cdot}O{\cdot}$ radicals. Reaction (7) requires that 50% or more of the peroxide shall be converted into benzoic acid. In fact, Cosgrove and Waters obtained 65% with *p*-methoxyphenol and yields ranging from 55 to 100% with nine other phenols.

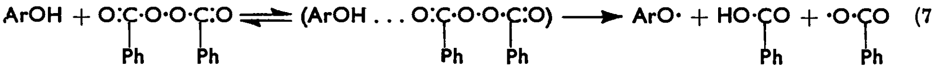
At first sight reaction (7) may appear improbable on energetic grounds, but the following calculation shows that it is approximately thermo-neutral. The heat of reaction is given by :

$$\Delta H = [\Delta H_f(\mathrm{BzO\cdot}) - \Delta H_f(\mathrm{Bz_2O_2})] + [\Delta H_f(\mathrm{ArO\cdot}) - \Delta H_f(\mathrm{ArOH})] + \Delta H_f(\mathrm{BzOH}) \quad \text{(iii)}$$

$$= \tfrac{1}{2}[D_{\mathrm{BzO-OBz}} - \Delta H_f(\mathrm{Bz_2O_2})] + [D_{\mathrm{ArO-H}} - \Delta H_f(\mathrm{H\cdot})] + \Delta H_f(\mathrm{BzOH}) \quad . \quad . \quad \text{(iv)}$$

where the symbols have their usual significance. Heats of solution are unlikely to alter the value of ΔH by more than *ca.* 3 kcal. and will therefore be neglected. The following values : $\Delta H_f(\mathrm{Bz_2O_2}) = -93{\cdot}5$ (Breitenbach and Derkosch [20]), $\Delta H_f(\mathrm{H\cdot}) = 52$ (Cottrell [21]), $\Delta H_f(\mathrm{BzOH}) = 92$ (from heat of combination : Prosen and Rossini [22]), $D_{\mathrm{BzO-OBz}} = 30$ (Swain *et al.*,[7] Bawn and Mellish [15]) and $D_{\mathrm{ArO-H}} = 84$ kcal. mole^{-1} (value for unsubstituted phenol calculated from the oxidation–reduction potential [23]), when substituted in equation (iii) yield the value 2 kcal. for ΔH. The least accurate of the above data is presumably the value for $D_{\mathrm{ArO-H}}$, but this is unlikely to be sufficiently in error [23] for ΔH to exceed the activation energy of 20 kcal. found by Tipper [4] for phenol or even the value of 11 kcal. for *p*-methoxyphenol found in this work. The assumption of reaction (7) therefore does not conflict with thermochemical data. Additional evidence for this reaction is provided by the effects of the structure of the phenol on the rate.[16]

It is not unlikely that reaction (7) is preceded by the formation of a hydrogen bond between the phenol and the carbonyl oxygen atom. Phenol molecules readily form hydrogen bonds with acceptor groups.[24] This would explain the fact that the rate is lower in dioxan (Fig. 5) and acetophenone than in benzene (Fig. 4), since the former solvents can compete more effectively with the peroxide in the formation of association complexes with the phenol. In an analogous case [25] association between phenol and dioxan is sufficiently strong to prevent the phenol from reacting with *tert.*-butyl chloride. It is suggested that the present reaction occurs *via* the decomposition of a hydrogen-bonded complex present in equilibrium concentration :



$$\mathrm{ArOH} + \mathrm{O{:}\underset{Ph}{C}{\cdot}O{\cdot}O{\cdot}\underset{Ph}{C}{:}O} \rightleftharpoons (\mathrm{ArOH} \ldots \mathrm{O{:}\underset{Ph}{C}{\cdot}O{\cdot}O{\cdot}\underset{Ph}{C}{:}O}) \longrightarrow \mathrm{ArO\cdot} + \mathrm{HO{\cdot}\underset{Ph}{C}O} + \mathrm{{\cdot}O{\cdot}\underset{Ph}{C}O} \quad (7a)$$

This would give rise to second-order kinetics. Evidence for a similar type of reaction has been found by Bateman and Hughes [26] in the thermal decomposition of alkenyl hydro-

---

[20] Breitenbach and Derkosch, *Monatsh.*, 1951, **82**, 177.

[21] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1954.

[22] Prosen and Rossini, *Bur. Stand. J. Res.*, 1944, **33**, 439.

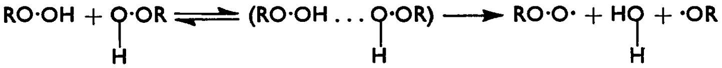
[23] Hush, *J.*, 1953, 2375.

[24] Lüttke and Mecke, *Z. Elektrochem.*, 1949, **53**, 241.

[25] Hart, Cassis, and Bordeaux, *J. Amer. Chem. Soc.*, 1954, **76**, 1639.

[26] Bateman and Hughes, *J.*, 1952, 4594.

peroxides. These decompose by a second-order reaction which Bateman and Hughes consider to take place as follows :



$$\mathrm{RO{\cdot}OH} + \underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}\mathrm{{\cdot}OR} \rightleftharpoons (\mathrm{RO{\cdot}OH}\ldots\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}\mathrm{{\cdot}OR}) \longrightarrow \mathrm{RO{\cdot}O{\cdot}} + \mathrm{H}\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}} + \mathrm{{\cdot}OR}$$

It is more difficult to account for the deviations from second-order kinetics which are most appreciable at 30° (Figs. 6 and 7). The disappearance of the effect at higher temperatures suggests that it also is due to some kind of association. Self-association of the phenol, however, does not explain the kinetics observed. These can be partly accounted for if it is assumed that a complex formed from a peroxide molecule and two phenol molecules is present in appreciable concentration and decomposes more rapidly than the 1 : 1 complex, but further investigation of the point is required. Some obscurity in the details of the initial interaction, however, does not affect the main conclusion that the reaction occurs directly between peroxide and phenol molecules and therefore does not depend on the preliminary dissociation of the peroxide or on the propagation of chains.

The assistance of Mr. D. T. Broberg with part of the analytical work described in this and the following paper is gratefully acknowledged. The authors also thank Dr. R. D. Brown for helpful discussion and Messrs. Timbrol Ltd. for the gift of chemicals.

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION,
DIVISION OF TRIBOPHYSICS, UNIVERSITY OF MELBOURNE,
CARLTON, N.3, VICTORIA, AUSTRALIA.

[*Received, November 7th,* 1955.]