573. *Structural Effects in the Reaction between Benzoyl Peroxide and Phenols.*

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The rate of the direct reaction between a phenol and benzoyl peroxide increases with decreasing strength of the O–H bond. This supports the view that the reaction occurs by homolytic transfer of the phenolic hydrogen atom to the carbonyl atom of the peroxide. Additional support is provided by the fact that steric effects which limit the accessibility of the hydrogen atom cause a decrease in the rate.

The efficiency of a phenol in retarding the chain decomposition of benzoyl peroxide induced by dioxan increases as the O–H bond strength decreases.

THE preceding paper showed that the reaction between comparable concentrations of benzoyl peroxide and *p*-methoxyphenol in an inert solvent occurs mainly by direct interaction of the phenol and peroxide molecules. It was suggested that the reaction occurs by the transfer of the phenolic hydrogen atom to the carbonyl oxygen atom of the peroxide:

$$\mathrm{ArOH + Ph{\cdot}CO{\cdot}O{-}O{\cdot}COPh \longrightarrow ArO{\cdot} + Ph{\cdot}CO{\cdot}OH + {\cdot}O{\cdot}COPh} \quad . \; . \; . \quad (1)$$

This involves rupture of the O–H bond of the phenol and the O–O bond of the peroxide, with formation of a molecule of benzoic acid. Since of these processes only the first depends on the structure of the phenol, the rate of reaction of the peroxide with different phenols would be expected to increase with decreasing strength of the O–H bond. This paper describes an investigation of the effect of the structure of the phenol on the rate of reaction, carried out with the object of testing this conclusion.

A measure of the strength of the O–H bond is given by the "critical oxidation potential" (E_c) of the phenol as defined by Fieser,[2] a high value of E_c corresponding to a high bond strength (cf. p. 2960). The reaction rate should therefore increase with decreasing E_c. The efficiency of a phenol as an antioxidant increases with decreasing

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[1] Batten and Mulcahy, preceding paper.

[2] Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5204; see also refs. 3 and 4.

E_c.[3, 5] This undoubtedly reflects the influence of the O–H bond strength on the rate of the reaction

$$\mathrm{ArOH} + \mathrm{R}\cdot \longrightarrow \mathrm{ArO}\cdot + \mathrm{RH} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

the oxidation chains being propagated by R· but not by ArO· radicals. The chain decomposition of benzoyl peroxide which occurs in a reactive solvent such as dioxan is also retarded by phenols. This probably arises from a reaction similar to (2) where R· is now the benzoate radical or a solvent radical [cf. equations (1) and (2) of preceding paper]. It follows that the rate at which a phenol reacts directly with the peroxide should increase in a parallel fashion with its efficiency in retarding the chain decomposition. The two effects can be compared directly by studying the overall rate of disappearance of the peroxide from a reactive solvent over a range of phenol concentrations. As already shown,[1] the retarding effect on the chain decomposition can be investigated at low phenol concentrations, and the rate of the direct reaction at high concentrations. In an unreactive solvent, on the other hand, the direct reaction is predominant over almost the whole concentration range, but the comparison with the retarding efficiency of the phenol is not available. Moreover, as indicated previously, the immiscibility of such solvents with water introduces difficulties in the analysis which limit the number of phenols suitable for study. Experiments have been carried out with several phenols in three unreactive solvents and with about 20 phenols in dioxan. The results establish that the rate of reaction of a phenol with the peroxide and its retarding effect on the induced decomposition are in fact related. In general, the activity of the phenol in both reactions depends on its critical oxidation potential in the expected manner but in some cases steric factors become predominant.

Experimental.—Solutions of benzoyl peroxide of constant concentration (50 mM) were allowed to react for a fixed time (135 min.) at 80·65° in the presence of various concentrations of the several phenols, and then analysed for peroxide. The amount of peroxide which had disappeared was taken as a semi-quantitative measure of the overall rate of reaction. The experimental procedure, analytical methods, and purification of solvents are described in the preceding paper. The phenols (and other substances used) were commercial specimens purified by conventional methods. M.p.s agreed well with values in the literature (with three exceptions: *o*-cresol, m. p. 29—30°; *m*-cresol, m. p. 10—11°; and 1-naphthylamine, m. p. 47—48°).

RESULTS AND DISCUSSION

Figs. 1—4 show the effects of several phenols on the amount of benzoyl peroxide which has reacted in the unreactive solvents benzene, acetophenone, and chloroform. The phenols differ widely in reactivity; for example, a concentration of 30 mM of 1-naphthol is sufficient to bring about complete reaction of the peroxide, whereas the effects of phenol and *p*-chlorophenol are inappreciable in the range of concentrations examined. Fig. 4 shows that very much greater concentrations of phenol are required to produce an effect comparable with that of 1-naphthol. *p*-Methoxyphenol and 2 : 4 : 6-trimethylphenol are of intermediate activity.

The effects of a wider range of phenols on the rate of disappearance of the peroxide from dioxan are shown in Figs. 5*a*—*d*. Retardation of the solvent-induced chain decomposition is shown by a decrease, and the effect of the direct reaction by an increase, in the amount of peroxide which has reacted. Both effects are sensitive to the structure of the phenol. Furthermore, the phenols which show a strong retarding effect at low concentrations are, in general, those with which the reaction of the peroxide at higher concentrations is most rapid. This is exemplified by the behaviour of 1-naphthol (Fig. 5*a*), 2 : 4 : 6-trimethylphenol (Fig. 5*b*), and 2 : 6-dimethoxyphenol (Fig. 5*c*). On the other hand, with phenols such as *p*-chlorophenol, phenol itself (Fig. 5*a*), or the cresols (Fig. 5*b*) which retard only feebly, there is no sign of an increased rate at higher concentrations in the range examined. The order of activity of the different phenols in the direct reaction is the same as that found with the unreactive solvents. This shows incidentally that the weak retardation observed

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[3] Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 252.
[4] Hush, *J.*, 1953, 2375.
[5] Lowrey, Egloff, Morrell, and Dryer, *Ind. Eng. Chem.*, 1933, **25**, 804.

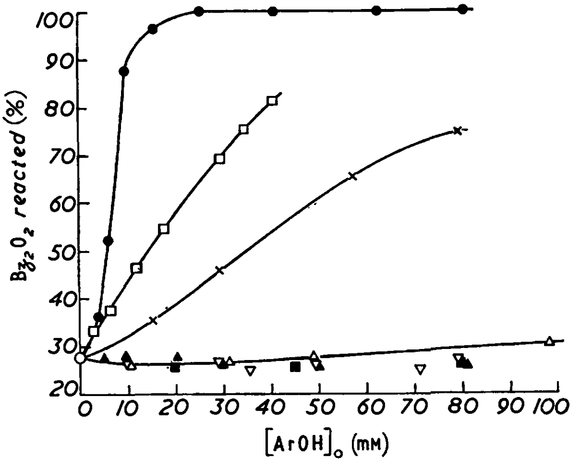

FIG. 1. *Effects of initial concentrations of various phenols on the total amount of benzoyl peroxide which has reacted in benzene.*

- ● 1-Naphthol.
- □ *p*-Methoxyphenol.
- × 2 : 4 : 6-Trimethylphenol.
- ▲ *p*-Chlorophenol.
- ▽ Phenol.
- △ *o*-Methoxyphenol.
- ■ 2 : 6-Di-*tert*.-butyl-4-methylphenol.

The results given in this and subsequent figures (unless otherwise stated) were obtained at 80·65° with reaction time = 135 min., and initial benzoyl peroxide concentration = 50 mM.

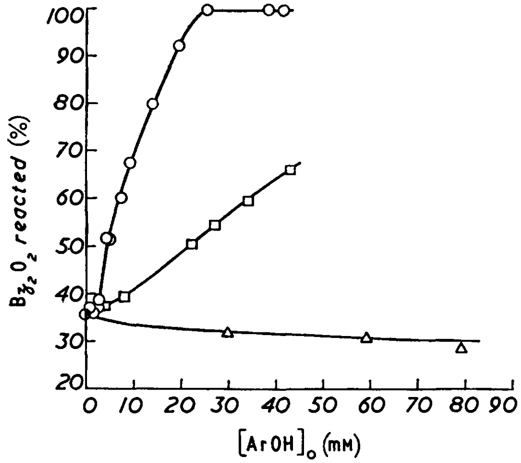

FIG. 2. *Effects of* (○) 1-*naphthol*, (□) p-*methoxyphenol, and* (△) *phenol on total amount of peroxide reacting in acetophenone.*

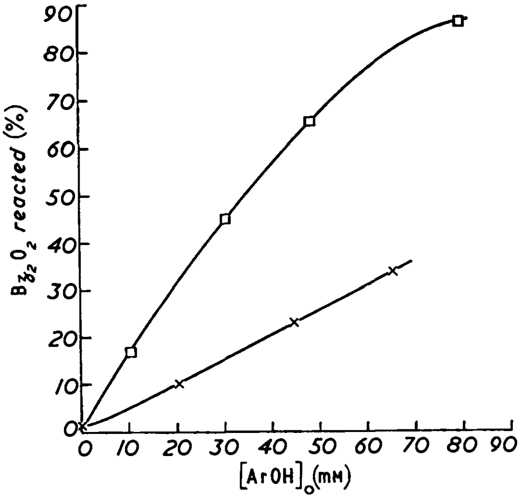

FIG. 3. *Effects of* (□) p-*methoxyphenol and* (×) 2 : 4 : 6-*trimethylphenol on total amount of peroxide reacting in chloroform*; $T = 60·3°$.

in dioxan with phenols such as phenol and *p*-chlorophenol is real and not the result of a strong retarding effect offset by relatively high activity in the direct reaction.

The efficiencies of the phenols as retarders and their activities in the direct reaction may be compared with their critical oxidation potentials E_c. This potential is an empirical quantity introduced by Fieser[2] as a relative estimate of the normal oxidation potential of the system

$$\mathrm{ArOH} \rightleftharpoons \mathrm{ArO}\cdot + \tfrac{1}{2}\mathrm{H}_2 \qquad \ldots\ldots\ldots \quad (3)$$

which generally cannot be measured under reversible conditions because of the reactivity of the ArO· radicals. The evidence for its validity has been discussed by Fieser[2] and by Hush.[4] It is probably safe for comparative purposes to regard it as a measure of the free-energy change in reaction (3) and therefore of the activity of the hydrogen atom in reactions involving severance of the O–H bond, *e.g.*,

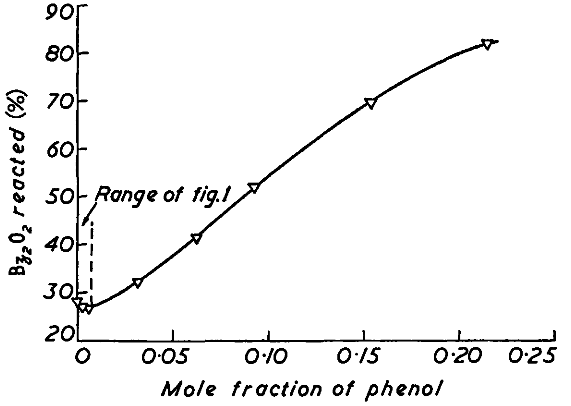

Fig. 4. *Effect of higher concentrations of phenol on total amount of peroxide reacting in benzene.*

$$\mathrm{ArOH} \longrightarrow \mathrm{ArO}\cdot + \mathrm{H}\cdot \qquad \ldots\ldots\ldots \quad (4)$$

or

$$\mathrm{ArOH} + \mathrm{X} \longrightarrow \mathrm{ArO}\cdot + \mathrm{XH} \qquad \ldots\ldots\ldots \quad (5)$$

where X is common to a series of reactions. If the entropy change in reaction (4) is assumed to be independent of the structure of ArOH, E_c can be considered to be a measure of the dissociation energy of the O–H bond.

The efficiencies (η) of the phenols as retarders, their activities in the direct reaction, and values of E_c are listed in the Table. The order is that of the retarding efficiency. The choice of the concentration at which to compare the retarding efficiencies is somewhat arbitrary : a high concentration is desirable to minimise the effects of consumption of the phenol and of possible retardation by products, but this is limited by the increasing rate of the direct reaction with increasing phenol concentration. A concentration of 15 mM was chosen as a reasonable compromise. The general order of activity, however, is not altered if the comparison is made at lower concentrations. The retarding efficiencies have been estimated by means of the expression

$$\eta = 100 \times (\Delta_0 - \Delta)/(\Delta_0 - \Delta_\infty)$$

where Δ_0, Δ, and Δ_∞ are respectively the amounts of peroxide which disappear in the absence of phenol, in the presence of 15 mM-phenol, and when the chain decomposition is completely inhibited, *e.g.*, by *p*-benzoquinone. The results do not permit more than a qualitative estimation of the relative activities of most of the phenols in the direct reaction. The phenols have been classified in three groups according to their behaviour in the concentration range shown in Figs. 1—3 and 5*a*—*d*. The values for E_c are from Fieser.[2] A clear correlation between η and E_c is evident in the Table. The significance of the individual values of η is limited by the approximate method of estimating the rate and probably in some cases by the occurrence of retardation by the products. Nevertheless, the correlation between η and E_c over the whole range is sufficiently close to leave little doubt that it represents a genuine property of the phenols. This shows that the retarding

FIG. 5. *Effects of initial concentrations of various phenols on the total amount of peroxide reacting in dioxan.*

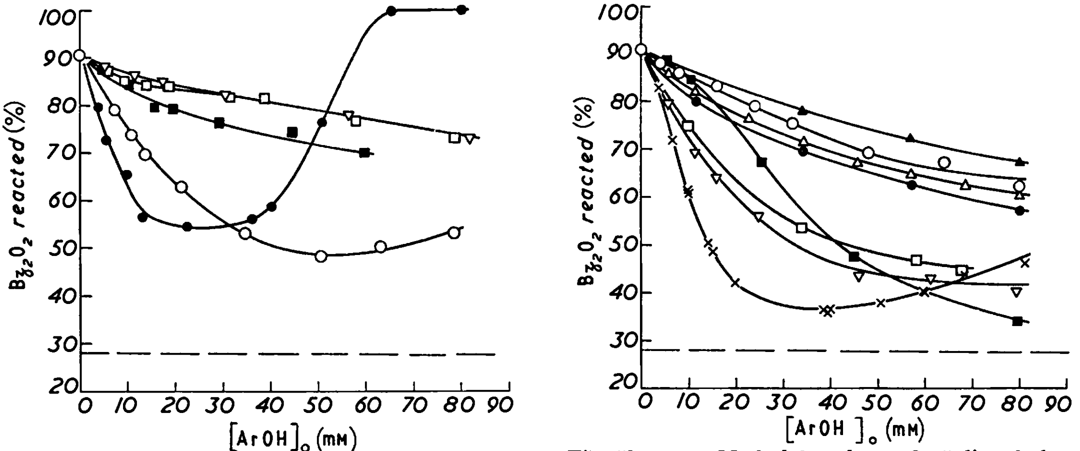

Fig. 5*a*: ▽, Phenol; □, *p*-chlorophenol; ■, 2 : 4 : 6-trichlorophenol; ○, 2-naphthol; ●, 1-naphthol.

Fig. 5*b*: ▲, *m*-Methylphenol; ○, 3 : 5-dimethylphenol; △, *p*-methylphenol; ●, *o*-methylphenol; □, 2 : 4-dimethylphenol; ▽, 2 : 6-dimethylphenol; ×, 2 : 4 : 6-trimethylphenol; ■, 2 : 6-di-*tert*.-butyl-4-methylphenol.

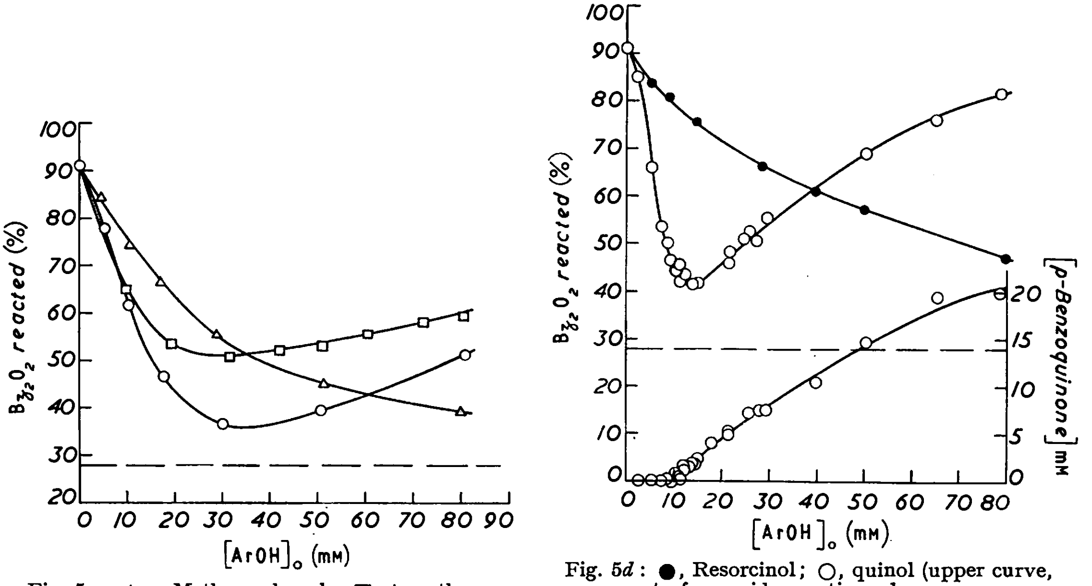

Fig. 5*c*: △, *o*-Methoxyphenol; □, *p*-methoxyphenol; ○, 2 : 6-dimethoxyphenol.

Fig. 5*d*: ●, Resorcinol; ○, quinol (upper curve, amount of peroxide reacting; lower curve, mM of *p*-benzoquinone in products).

efficiency in this as in other chain reactions depends on the facility with which the phenolic hydrogen atom can be abstracted, *i.e.*, on the strength of the O–H bond.

The Table shows that activity in the direct reaction runs parallel with the retarding efficiency, and therefore indicates that the rate of this reaction is also determined primarily by the strength of the O–H bond.* In agreement with this result the rates of the reaction in liquid phenol and in each of the three cresols [6] are in the opposite order from the values of E_c for these phenols. The influence of the structure of the phenol on its activity in the direct reaction thus supports reaction (1) as the rate-determining step.

Relative retarding efficiencies (η) *of phenols and rates of direct reaction with benzoyl peroxide compared with critical oxidation potentials* (E_c).

Phenol	E_c (v)	η	Activity in direct reaction	Phenol	E_c (v)	η	Activity in direct reaction
Quinol	0·65	—	Very active	Resorcinol	1·04	23	Inactive
2 : 4 : 6-Trimethylphenol	—	66	Active	*o*-Methylphenol	1·04	20	,,
2 : 6-Dimethoxyphenol	0·76	63	Very active	2 : 6-Di-*tert*.-butyl-4-methylphenol	—	(18)	,,
1-Naphthol	0·80	54	,,	*p*-Methylphenol	1·04	17	,,
p-Methoxyphenol	0·85	52	,,	2 : 4 : 6-Trichlorophenol	1·10	16	,,
2 : 6-Dimethylphenol	0·90	41	Active ?	3 : 5-Dimethylphenol	—	12	,,
2-Naphthol	1·02	36	Active	*m*-Methylphenol	1·08	10	,,
o-Methoxyphenol	0·87	35	Active ?	*p*-Chlorophenol	1·09	10	,,
2 : 4-Dimethylphenol	0·90	35	Inactive	Phenol	1·09	9	,,
p-Nitrophenol	1·43	74		2 : 4 : 6-Trinitrophenol	—	100	

Closer examination of the results reveals two interesting anomalies. The values of E_c for *o*- and *p*-methoxyphenol are almost the same but the *ortho*-compound is very much the less active (cf. Figs. 1 and 5*c*). The difference is evidently due to a steric effect. It is significant that the phenolic hydrogen atom in the *ortho*-compound forms an intramolecular hydrogen bond with the methoxy-group.[7] This apparently hinders the formation of the hydrogen bond between phenol and peroxide which, it was suggested in the preceding paper, precedes the transfer of the hydrogen atom. The effect is not evident with 2 : 6-dimethoxyphenol (Fig. 5*c*) probably because it is submerged in the increased activity caused by the second methoxy-group. The low activity of 2 : 6-di-*tert*.-butyl-4-methylphenol (Figs. 1 and 5*b*), which was noted by Cosgrove and Waters,[8] can also be ascribed to steric hindrance; E_c for this compound is not known but can be predicted to be at least as low as that of 2 : 4 : 6-trimethylphenol which, however, is considerably more active. The formation of intermolecular hydrogen bonds by 2 : 6-di-*tert*.-butyl-4-methylphenol is prevented [9] and its phenolic properties are strongly affected [10] by the large *tert*.-butyl groups adjacent to the hydroxyl group. It therefore seems safe to infer that these groups hinder the approach of the hydrogen atom to the peroxide molecule. The low activities of this compound and of *o*-methoxyphenol therefore lend added support to the view that the hydrogen atom is involved in the rate-determining step.

Steric effects evidently also influence the rate of reaction of the phenolic hydrogen atom with radicals. There is a similar but less marked discrepancy between the retarding effects of the *o*- and *p*-methoxyphenols on the chain decomposition (Fig. 5*c*). On the other hand, 2 : 6-di-*tert*.-butyl-4-methylphenol strongly retards the induced decomposition, and this is in line with its high activity as an anti-oxidant.[11] However, the results shown in Fig. 5*b* suggest that its kinetic behaviour is different from that of unhindered phenols.

Note on the Products of the Reaction in an Inert Solvent.—It was observed in the preceding paper that the products of the direct reaction between the peroxide and *p*-methoxyphenol or quinol cannot be distinguished without further investigation from those to be expected from unimolecular association of the peroxide followed by reaction of Ph·CO·O· radicals with the phenol. This is also the case with the products obtained by Cosgrove and Waters (cf. preceding paper) from the reactions of about ten phenols with the peroxide in boiling

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* No relation could be discerned between the rate and the ionisation constants of the phenols.

[6] Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1947, **69**, 2299.
[7] Wulf, Liddel, and Hendricks, *ibid.*, 1936, **58**, 2287.
[8] Cosgrove and Waters, *J.*, 1951, 388.
[9] Coggeshall, *J. Amer. Chem. Soc.*, 1947, **69**, 1620.
[10] Stillson, Sawyer, and Hunt, *ibid.*, 1945, **67**, 303.
[11] Rosenwald, Hoatson, and Chenicek, *Ind. Eng. Chem.*, 1950, **42**, 162.

chloroform. From the present work, however, it appears that under the conditions used by Cosgrove and Waters the direct reaction predominates even with the most inactive phenols. This is certainly the case with *p*-methoxyphenol (*A*) and 2 : 4 : 6-trimethylphenol (*B*) (cf. Fig. 3) and is at least highly probable with the less active 2 : 6-dimethylphenol (*C*). It is noteworthy that each of these three phenols gave a different type of product : *A* gave a compound of type (I) in 40% yield (based on the phenol), *B* gave >90% of a compound of type (II), and *C* gave 50% of the diphenoquinone corresponding to the diphenol (Type III) and 10% of the diphenol itself. The nature of the initial interaction between the peroxide and phenol being assumed to be the same in each case, it is difficult to see how the different products could be formed except as a result of subsequent radical-combination reactions as suggested in the preceding paper. Whether, in any particular case, like (ArO·) or unlike (ArO· and Ph·CO·O·) radicals combine no doubt depends on steric and other factors, but at all events the various products indicate that both kinds of radical are present. This is clearly compatible with the occurrence of reaction (1) as the initial step in the reaction.

FIG. 6. *Effects of* (●) p-*nitrophenol,* (○) 2 : 4 : 6-*tri-nitrophenol, and* (□) 1 : 3 : 5-*trinitrobenzene on total amount of peroxide reacting in dioxan.*

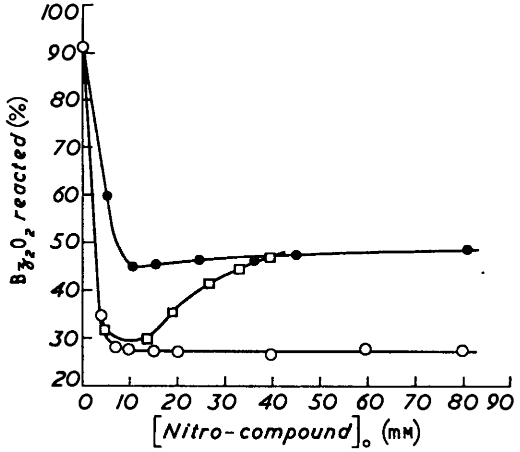
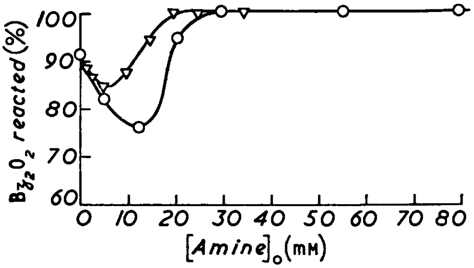


FIG. 7. *Effects of* (○) 1-*naphthylamine and* (△) NN-*dimethyl*-1-*naphthylamine on total amount of peroxide reacting in dioxan.*



Some Other Observations.—The nitrophenols (Table and Fig. 6) are outstanding exceptions to the correlation between η and E_c. However, 1 : 3 : 5-trinitrobenzene is a strong retarder (Fig. 6) and it is therefore clear that the retarding effect of nitrophenols is mainly due to the nitro-groups. 2 : 4 : 6-Trinitrophenol reduces the rate to the limit found with *p*-benzoquinone.[1] The unexpectedly different behaviour of 1 : 3 : 5-trinitrobenzene and *p*-nitrophenol is believed to be genuine but the point has not been pursued. The value of η for quinol (79) is omitted from the Table because the retardation is known to be caused partly by the product, *p*-benzoquinone (cf. Fig. 5*d*). In spite of numerous attempts, reproducible results could not be obtained with catechol. This was shown not to be due to traces of air or water or to be peculiar to one method of purification of the catechol but was not investigated further.

The conclusion that benzoyl peroxide reacts directly with phenols suggests a comparison with its reaction with aromatic amines. A few experiments were carried out with 1-naphthylamine and *NN*-dimethyl-1-naphthylamine in dioxan (Fig. 7). The behaviour is at least superficially similar to that of the phenols and, in agreement with the evidence produced by Nozaki and Bartlett,[6,12] it appears that the primary amine is more reactive than the corresponding phenol (1-naphthol, Fig. 5*a*). However, the high reactivity of *NN*-dimethyl-1-naphthylamine and other tertiary amines [13] has no counterpart in the

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

[13] Horner and Schwenk, *Annalen*, 1950, **566**, 69.

phenolic ethers.[14,15] The reaction with tertiary amines is a second-order reaction,[6,16] which according to Horner and Schwenk [13,17] involves a one-electron transfer from amine to peroxide. Horner and Schwenk consider that the reaction with primary and secondary amines occurs in a similar way, but analogy with the phenols suggests that in these cases it may occur at least partly by hydrogen transfer.

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[14] Horner and Scherf, *Annalen*, 1951, **573**, 35.

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

[16] Meltzer and Tobolsky, *J. Amer. Chem. Soc.*, 1954, **76**, 5178.

[17] Horner and Schwenk, *Angew. Chem.*, 1949, **61**, 411.