455. *The Retardation of Benzaldehyde Autoxidation. Part III.** *A Kinetic Study of the Actions of* 3 : 5 : 3′ : 5′-*Tetramethyl*-4 : 4′-*diphenoquinone and the Corresponding Quinol.*

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The retarding effects of the above-mentioned diphenoquinone and -quinol upon the benzoyl peroxide-catalysed autoxidation of benzaldehyde have been studied kinetically. It is concluded that the quinone acts as a chain-stopping agent by combining with free benzoyl radicals :

$$\text{Ph·CO·} + \text{Q} \longrightarrow \text{Ph·CO·Q·};\ \text{Ph·CO·Q·} + \text{Ph·CO·} \longrightarrow \text{Ph·CO·Q·COPh}$$

The quinol is first dehydrogenated to the quinone and eventually yields the same chain-ending product :

$$\text{Ph·CO·} + \text{H}_2\text{Q} \longrightarrow \text{Ph·CHO} + \text{HQ·};\ \text{Ph·CO·} + \text{HQ·} \longrightarrow \text{Ph·CHO} + \text{Q}$$

The kinetic analysis excludes other chain-termination mechanisms except when the chain-starting catalyst is present in large excess.

In Part II * it was shown that red 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone acted as a chain terminator towards the benzoyl peroxide-catalysed autoxidation of benzaldehyde, and was converted by a combination process into comparatively colourless products which had very little, if any, retarding action.

Now the quinone (Q) may terminate the reaction chain (3), (4) †

$$\text{Ph·CO·} + \text{O}_2 \longrightarrow \text{Ph·CO·O}_2\text{·} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{Ph·CO·O}_2\text{·} + \text{Ph·CHO} \longrightarrow \text{Ph·CO·O·OH} + \text{Ph·CO·} \quad . \quad . \quad . \quad (4)$$

by any one of the three following ways, or by any combination of them :

(i) The quinone may destroy the chain-starting catalyst

$$\text{Ph·CO·O–O·COPh} \longrightarrow 2\text{Ph·CO}_2\text{·} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Ph·CO}_2\text{·} + \text{Q} \longrightarrow \text{Inert products}$$

In this case the quinone should be a complete inhibitor of any autoxidation until it has been used up, at which time a fast unretarded oxygen uptake should set in : this does not occur (compare Fig. 5 of Part II).

(ii) The quinone may combine with the benzoyl radical, Ph·CO· :

$$\text{Ph·CO·} + \text{Q} \longrightarrow \text{Ph·CO·Q·} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13'a)$$

If (13′*a*) were followed by (13′*b*), as probably does occur, then the kinetics of the

$$\text{Ph·CO·Q·} + \text{Ph·CO·} \longrightarrow \text{Ph·CO·Q·CO·Ph} \quad . \quad . \quad . \quad . \quad (13'b)$$

autoxidation would not be affected.

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* Part II, preceding paper. † For numbering of reactions see Part I, *J.*, 1951, 812.

(iii) The quinone may combine with the benzoylperoxy-radical, $\mathrm{Ph{\cdot}CO{\cdot}O_2{\cdot}}$, by reaction (14′) or more probably (14′*a*)

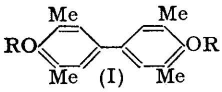
$$\mathrm{Ph{\cdot}CO_3{\cdot} + Q \longrightarrow Ph{\cdot}CO_3{\cdot}Q{\cdot}} \qquad (14')$$

$$\mathrm{Ph{\cdot}CO{\cdot}O_2{\cdot} + Q \longrightarrow Ph{\cdot}CO{\cdot}Q{\cdot} + O_2} \qquad (14'a)$$

and again this could be followed by (14′*b*) without affecting the kinetics:

$$\mathrm{Ph{\cdot}CO{\cdot}Q{\cdot} + Ph{\cdot}CO{\cdot}O_2{\cdot} \longrightarrow Ph{\cdot}CO{\cdot}Q{\cdot}COPh + O_2} \qquad (14'b)$$

From both (ii) and (iii) the likely product is 4 : 4′-dibenzoyloxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl (I; R = COPh). This colourless substance has been prepared and has been found not to be a retarder of the autoxidation of benzaldehyde (cf. Part IV, *J.*, 1952, 2432).



(I)

Now from the steady-state relationships

$$k_3[\mathrm{Ph{\cdot}CO{\cdot}}][\mathrm{O_2}] = k_4[\mathrm{Ph{\cdot}CO_3{\cdot}}][\mathrm{Ph{\cdot}CHO}]$$

and

$$2k_1[\text{Benzoyl peroxide}] = k_t[\text{Quinone}][\mathrm{R{\cdot}}]$$

(where R· is the radical which combines with the quinone) which should hold under the conditions of initial reaction, it follows that if chain ending occurs by process (ii) then

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{2k_1[\text{Benzoyl peroxide}]}{k_t[\text{Quinone}]} \times k_3[\mathrm{O_2}] \qquad (A)$$

whilst if chain ending occurs by process (iii), reaction (14′*a*), then

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{2k_1[\text{Benzoyl peroxide}]}{k_t[\text{Quinone}]} \times k_4[\text{Benzaldehyde}] \qquad (B)$$

If both processes (ii) and (iii) occur, then

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{2k_1[\text{Benzoyl peroxide}]}{k_t[\text{Quinone}]} \times \{k_3[\mathrm{O_2}] + k_4[\text{Benzaldehyde}]\} \qquad (C)$$

If chain endings by processes (i) and (ii) occur concurrently, then

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{2k_1k_3[\text{Benzoyl peroxide}][\mathrm{O_2}]}{k_t[\text{Quinone}]} \times \frac{k_2[\text{Benzaldehyde}]}{k_2[\text{Benzaldehyde}] + k_t[\text{Quinone}]} \qquad (D)$$

(D) approximates to (A) if nearly all the radicals from the benzoyl peroxide react with the benzaldehyde and start reaction chains, and to

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{2k_1k_2k_3[\text{Benzoyl peroxide}][\mathrm{O_2}][\text{Benzaldehyde}]}{k_t[\text{Quinone}]^2} \qquad (E)$$

if nearly all the $\mathrm{Ph{\cdot}CO_2{\cdot}}$ radicals react with the quinone.

The relationships (A)—(E) are so different that a kinetic study of the order of the reaction with respect to each component, under conditions of fairly long chain length, should reveal the chemical natures of the radicals which combine with the quinone. This investigation has been carried out.

The first-order dependence on benzoyl peroxide at 79·7° has been instanced in Part II (*loc. cit.*). Table 1 shows that this relationship also holds at 60°. Fig. 1 shows that both at 60° and 80° the inverse of the rate of oxygen uptake is so closely dependent on the quinone concentration that relationship (E), or more significantly chain ending by process (i), can be eliminated. Fig. 2 shows that at both temperatures the

TABLE 1. *Effect of benzoyl peroxide on the autoxidation rate at* 60°.

(Each mixture contained 1·5 g. of benzoic acid and 2·5 mg. of tetramethyldiphenoquinone in 10 ml. of benzaldehyde.)

Benzoyl peroxide (mg.)	20	30	40	50	60	70	80	90
$\mathrm{O_2}$ uptake rate for first 10 min. (ml./min.)	0·214	0·281	0·384	0·473	0·551	0·613	0·768	0·859
10^4 Rate/[Benzoyl peroxide]	107	94	98	95	92	88	96	95

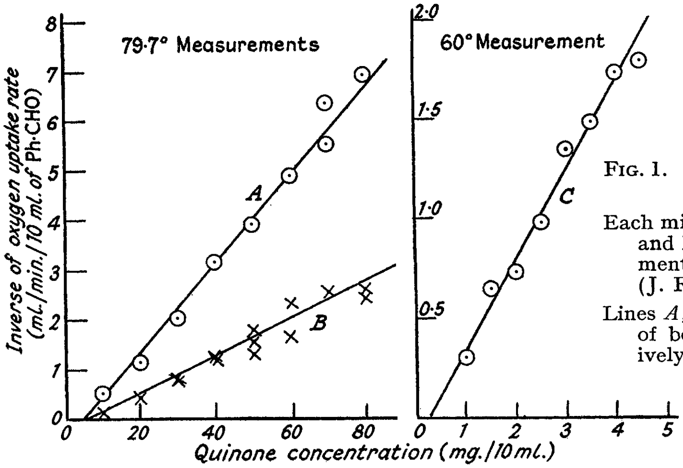


FIG. 1. *Dependence of autoxidation rate on quinone concentration.*

Each mixture contained 1·5 g. of $Ph\cdot CO_2H$ and 10 ml. of Ph·CHO. 79·7° Measurements (C. W.-J.), 60° measurements (J. R. D.).

Lines *A*, *B*, *C* : 0·050, 0·150, and 0·100 g. of benzoyl peroxide catalyst, respectively.

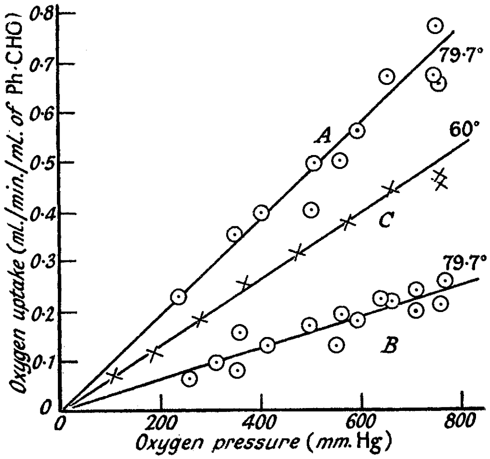


FIG. 2. *Dependence of autoxidation rate on oxygen pressure.*

Each mixture contained 1·5 g. of $Ph\cdot CO_2H$ and 10 ml. of Ph·CHO. 79·7° Measurements (C. W.-J.), 60° measurements (J. R. D.).

Lines *A*, *B* : 0·150 and 0·050 g. of benzoyl peroxide, respectively, and 0·050 g. of quinone.

Line *C*: 0·100 g. of benzoyl peroxide and 0·005 g. of quinone.

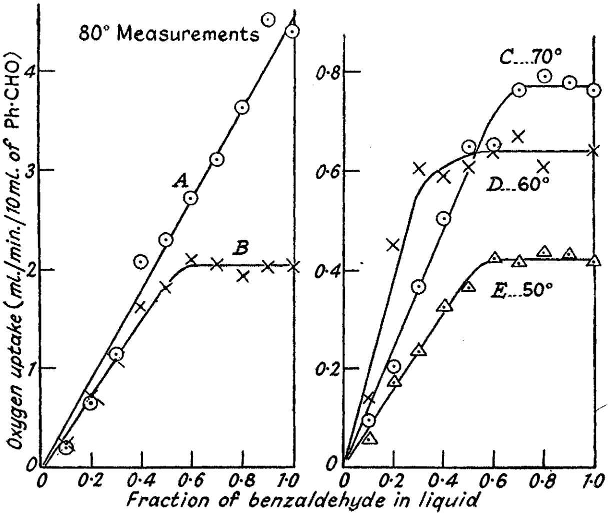


FIG. 3. *Autoxidation rates of benzaldehyde–chlorobenzene mixtures.*

Each mixture contained 1·5 g. of $Ph\cdot CO_2H$ and 10 ml. of mixed solvent.

Line	$(Ph\cdot CO\cdot O)_2$, g.	Quinone, g.
A	0·30	0·030
B	0·05	0·010
C	0·25	0·020
D	0·10	0·005
E	0·50	0·005

rate of oxidation is proportional to the first power of the oxygen concentration. This could be taken as conclusive evidence that the chain ending occurs by process (ii) alone, were it not for the fact that, as line *A* of Fig. 3 shows, in our first measurements at 80°, which have been shown to be reproducible, the rate of oxidation of benzaldehyde–chlorobenzene mixtures appeared to indicate a simple first-order dependence on the concentration of the benzaldehyde. However, when one of us (J. R. D.), after confirming this result, repeated the kinetic study at lower temperatures, and then even at 80° using a lower benzoyl peroxide concentration, it was found that, although the strict first-order dependence of the oxygen uptake rate on benzoyl peroxide concentration and on oxygen pressure remained exact to well within the accuracy of the rate measurements, yet the relationship between the rate and the composition of benzaldehyde–chlorobenzene mixtures showed a decided inflexion as the lines *B* to *E* of Fig. 3 show, and at high benzaldehyde percentages became independent of the composition of the solvent mixture. We conclude, therefore, that in mixtures of high benzaldehyde concentration, chain ending chiefly occurs by combination of benzoyl (Ph•CO•) radicals with the quinone, as indicated by scheme (ii). To account for the dependence of the rate of autoxidation on the composition of the solvent under certain conditions, we suggest, very tentatively, that with high chlorobenzene concentrations in solutions containing much more catalyst than inhibitor some of the benzoate (Ph•CO₂•) radicals may react with the chlorobenzene, perhaps as such, *e.g.*,

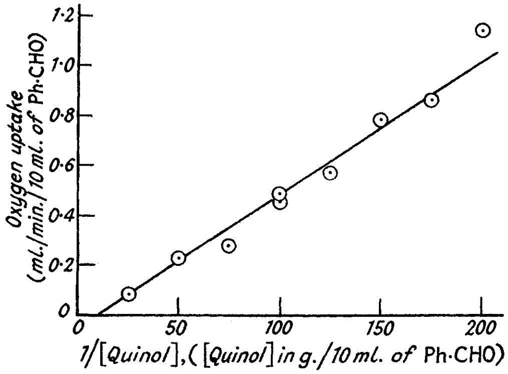


FIG. 4. *Relationship between autoxidation rate and inverse of the quinol concentration. (Temp. 60°.)*

Each mixture contained 1·5 g. of $Ph{\cdot}CO_2H$ and 0·250 g. of benzoyl peroxide in 10 ml. of benzaldehyde.

$$Ph{\cdot}CO_2{\cdot} + C_6H_5Cl \longrightarrow Ph{\cdot}CO_2H + {\cdot}C_6H_4Cl$$

or, more probably, after decomposition to more active phenyl radicals:

$$Ph{\cdot} + C_6H_5Cl \longrightarrow Ph{\cdot}C_6H_4Cl + H{\cdot}$$

the latter course being more favoured at elevated temperatures. One must suppose that these radicals do not start autoxidation chains but are destroyed by more direct reaction with the quinone. The dependence of the rate of decomposition of benzoyl peroxide on the nature of the solvent (Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216), which has already been considered in Part II, may be a further contributing factor.

In Part II it was concluded that *m*-2-xylenol acted as a retarder of autoxidation by yielding first the dimer $(C_8H_9O{\cdot})_2$, probably 4 : 4′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl (I; R = H), which was then dehydrogenated to 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone. Fig. 4 shows that this quinol (I; R = H) is a retarder of autoxidation, and Table 2 shows that at constant composition the oxygen uptake rate is proportional to the oxygen pressure.

TABLE 2. *Effect of oxygen pressure on the retardation of benzaldehyde autoxidation by 4 : 4′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl.*

(Each solution contained 1·5 g. of benzoic acid, 0·25 g. of benzoyl peroxide, and 0·01 g. of the quinol in 10 ml. of benzaldehyde.)

O_2 pressure, cm. Hg	19·47	28·37	38·45	47·88	58·03	65·86	76·00
O_2 uptake, c.c./min., at N.T.P.	0·134	1·096	0·264	0·291	0·381	0·383	0·497
10^5 Rate/Pressure	688	691	687	608	657	582	654

Fig. 5 shows that the autoxidation rate is proportional to the first power of the catalyst concentration, though the plot does not pass through the origin. From Fig. 5 the oxidation rate (in ml. min.$^{-1}$ l.$^{-1}$ of Ph·CHO) is

$$-d[O_2]/dt = (0{\cdot}18[\text{Benzoyl peroxide}] + 0{\cdot}06)/[\text{Quinol}]$$

whilst the corresponding value for the quinone retarder oxidation (in the same units) is

$$-d[O_2]/dt = 0{\cdot}24[\text{Benzoyl peroxide}]/[\text{Quinone}]$$

where the weights of both catalyst and retarder are given in grams.

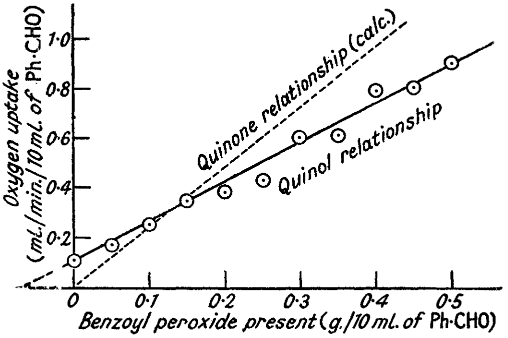


FIG. 5. *Dependence of autoxidation rate upon benzoyl peroxide concentration.* (*Temp.* 60°.)

Full line, —⊙——⊙—. Experimental results for 0·010 g. of quinol and 1·5 g. of Ph·CO$_2$H in 10 ml. of benzaldehyde.

Broken line. Relationship for a similar weight of the quinone calculated from the data of Table 1.

The first-order dependence on benzoyl peroxide concentration shows that the quinol, like the quinone, acts as a chain terminator by a combination mechanism. This accords with the scheme

$$R\cdot + H_2Q \longrightarrow R{-}H + HQ\cdot;\ R\cdot + HQ\cdot \longrightarrow R{-}H + Q$$

followed by

$$R\cdot + Q \longrightarrow RQ\cdot;\ RQ\cdot + R\cdot \longrightarrow R{-}Q{-}R$$

From the experimental relationships above it can be seen that at low benzoyl peroxide concentrations the quinone is the better retarder but at high catalyst concentrations the quinol is the more effective. Though from the mechanism given above it might be expected that the quinol would be twice as effective as the quinone this is not the case, and consequently part of it must be oxidised by other means, *e.g.*, by direct reaction with oxygen, perbenzoic acid, or with the chain-initiating benzoyl radicals.

Were the initial oxidation of the quinol due to the benzoate (Ph·CO$_2$·) radicals alone, then in quinol–benzoyl peroxide mixtures there would be no autoxidation unless an excess of benzoyl peroxide were present, and this is not the case. Though the solid quinol is stable in dry air it soon becomes red when kept in solution. Solutions of the quinol in both benzaldehyde and chlorobenzene rapidly oxidised at 60° under a nitrogen atmosphere upon the addition of benzoyl peroxide, so the direct reaction $Ph{\cdot}CO_2{\cdot} + H_2Q \longrightarrow Ph{\cdot}CO_2H + HQ{\cdot}$ does occur to an appreciable extent. On account of the direct oxidation of the quinol there can be little chance of its attaining a significant concentration in the autoxidising benzaldehyde–*m*-2-xylenol system.

Experimental.—The purification of materials and the oxygen uptake measurements were carried out by the procedure described in Part I (*loc. cit.*). We thank Mr. R. F. Moore for assistance in preparing pure samples of 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone and the corresponding quinol.

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