454. *The Retardation of Benzaldehyde Autoxidation. Part II.* A Comparative Study of the Actions of* p-*Cresol,* m-2-*Xylenol, and Their Oxidation Products.*

By William A. Waters and Charles Wickham-Jones.

A kinetic study shows that *m*-2-xylenol acts as a retarder of the benzoyl peroxide-catalysed autoxidation of benzaldehyde in exactly the same way as does *p*-cresol (see Part I *). The kinetic analysis of the autoxidising systems indicates that the phenolic retarders should eventually be converted into dimers of their respective radicals, $C_7H_7O\cdot$ and $C_8H_9O\cdot$, but, in the case of the system containing *p*-cresol, dimers $(C_7H_7O)_2$ do not seem to persist in the eventual reaction mixtures. With the *m*-2-xylenol system it has been established that the dimer $(C_8H_9O)_2$ is further oxidised to 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone, which has been isolated and estimated colorimetrically. This diphenoquinone is still a retarder of autoxidation, but it acts quite differently from the phenols in that it combines with active radicals present in the autoxidising benzaldehyde. Measurements of the rate of destruction of this diphenoquinone indicate that each molecule of it terminates two autoxidation chains.

In Part I * we showed that the effect of *p*-cresol on the rate of autoxidation of benzaldehyde could most simply be studied kinetically by (*a*) adding sufficient benzoic acid to bring about the rapid destruction of perbenzoic acid, and (*b*) using enough radical-producing catalyst (benzoyl peroxide) to reduce auto-catalytic chain starting to a very small and effectively constant value. Under these conditions the liquid-phase autoxidation of benzaldehyde containing a little *p*-cresol proceeds in the dark at an almost constant rate for a long time and it was inferred that the *p*-cresol acted mainly as a chain-transfer agent. Since the rate of oxygen uptake was very nearly proportional to the product [Benzaldehyde]^2[Benzoyl peroxide]$^{\frac{1}{2}}$[*p*-Cresol]$^{-1}$, it was concluded that the main chain-ending process was a dimerisation, or possibly a disproportionation, of *p*-tolyloxy-radicals :

$$2(C_7H_7O\cdot) \longrightarrow \text{Inert products} \quad . \; . \; . \; . \; . \quad (1)$$

In order to substantiate this deduction from chemical kinetics we have attempted to isolate from our autoxidised mixtures the phenolic and ketonic products $(C_7H_7O)_2$, (I) and

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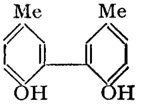
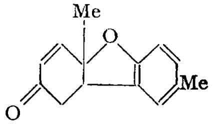
* *J.*, 1951, 812, is regarded as Part I of this series.

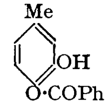
(II), which Cosgrove and Waters (*J.*, 1951, 1726) had obtained from *p*-cresol by direct oxidation with hydroxyl radicals. However, neither these dimers, nor 4-benzoyloxy-*m*-cresol (III), which is the direct reaction product from benzoyl peroxide and *p*-cresol (*idem, J.*, 1949, 3189), nor even *s*-diphenylethylene dibenzoate, which is formed by the direct action of benzoyl peroxide on benzaldehyde (Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258), could be separated in identifiable amounts. Apart from unchanged materials and much benzoic acid, the eventual residues from several reactions were brownish polymers (*M*, 700—800) which could be separated into phenolic and non-phenolic fractions, neither of which was crystalline. Now, the main dimer $(C_7H_7O)_2$ which results from the free-radical oxidation of *p*-cresol is 3 : 3′-di-*p*-cresol (I) and, since it is phenolic, this, as also (III), would be expected to be a retarder of autoxidation that would eventually be destroyed by such a reaction.



(I)



(II)



(III)

Kinetic measurements showed that in equimolar conditions, with identical amounts of catalyst, (I) gave an oxygen uptake rate of about 0·35 of that attained with *p*-cresol, though (III) gave about 2·5 times as great, and (II) about 7 times as great an oxidation rate.

The above suffices to show why the compounds (I)—(III), if formed, are not the end-products of the destruction of *p*-cresol by the reaction scheme proposed in Part I. It indicates, too, that this scheme must now be regarded as the course of the first stage only in the role of *p*-cresol as a retarder of benzaldehyde autoxidation. Since subsequent chain reactions involving reaction products such as (I)—(III) would also have chain-ending velocities dependent on the concentration of the initial chain-starting catalyst, benzoyl peroxide, they are not revealed distinctly by the overall kinetic measurements.

The fact that chemically different products (I) and (II) may be formed in even the first stage of *p*-cresol oxidation inevitably complicates the elucidation of the complete sequence of reactions in this retarded autoxidation system. For this reason it then seemed to us that a comparative study of the retarding action of *m*-2-xylenol (IV) might be much more enlightening, since this phenol has both its *ortho*-positions blocked, and under conditions of free-radical oxidation it appears to yield chiefly 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone (VII) (Cosgrove and Waters, *J.*, 1951, 388, 1726). We therefore examined the benzoyl peroxide-catalysed autoxidation of benzaldehyde–*m*-2-xylenol mixtures containing benzoic acid, and this time chose the higher temperature of 79·7° for our kinetic measurements so as to be able to secure suitable initial oxygen uptake rates under conditions in which we could use easily weighable amounts of both xylenol and catalyst. We determined oxygen uptake rates for an initial period of 10 minutes only, since at this temperature the extent of the unimolecular decomposition of benzoyl peroxide is only about 2% during this period, according to the data of Swain, Stockmayer, and Clarke (*J. Amer. Chem. Soc.*, 1950, **72**, 5426), and thus during our measurements the rate of production of chain-starting radicals can be taken as constant. Over a longer period the rate of oxygen uptake decreased quite slowly, as in the *p*-cresol reaction described in detail in Part I. We did, for confirmation, repeat the series of measurements with the *p*-cresol–benzaldehyde system at 79·7° and verified that it had exactly the same kinetic characteristics as at 40°.

Fig. 1 shows that the rate of benzaldehyde autoxidation is very nearly proportional to $[m\text{-}2\text{-xylenol}]^{-1}$. In Fig. 2, curve *A* shows that the rate of oxygen absorption is proportional to the square root of the benzoyl peroxide concentration for high values of the latter only, whilst curve *B* shows that the more general relation

$$-\mathrm{d}[O_2]/\mathrm{d}t = k\{([Bz_2O_2] + b)^{\frac{1}{2}} - c\} \quad . \; . \; . \; . \; . \; . \; . \qquad (2)$$

holds for all concentrations of benzoyl peroxide, just as in the benzaldehyde-*p*-cresol system. Fig. 3 shows that for benzaldehyde-chlorobenzene mixtures the rate is proportional to the square of the benzaldehyde concentration, and Table 1 shows that

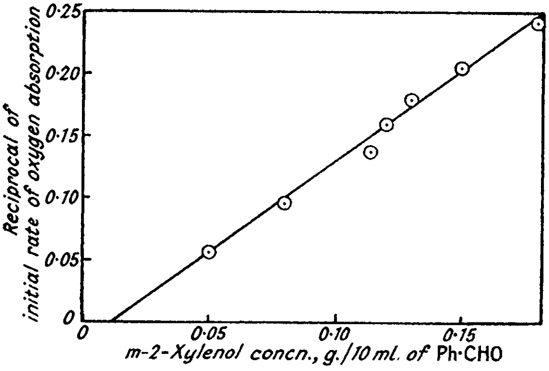
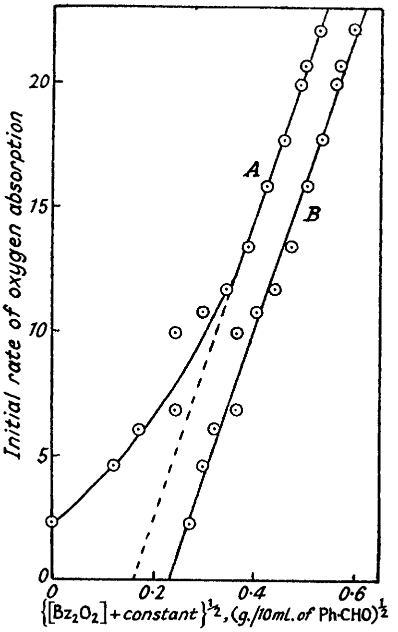


FIG. 1. *Initial oxygen absorption rates at* 79·7° *at different* m-2-*xylenol concentrations.*

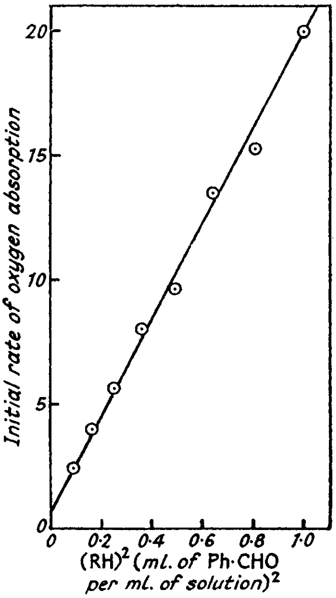
Initial rates of oxygen absorption in ml. of oxygen (at N.T.P.) per min. per mole of benzaldehyde. Initial concns. (in g./10 ml. of benzaldehyde): [Ph·CO_2H] = 1·50; [Bz_2O_2] = 0·1500.

FIG. 2. *Initial oxygen absorption rates at* 79·7° *at different benzoyl peroxide concentrations.*



Initial rates of oxygen absorption in ml. of oxygen (at N.T.P.) per min. per mole of benzaldehyde. Initial concns. (in g./10 ml. of benzaldehyde): [Ph·CO_2H] = 1·50; [*m*-2-xylenol] = 0·0600. Constant values (g. of benzoyl peroxide/10 ml. of benzaldehyde): Curve *A* 0; Curve *B* 0·075.

FIG. 3. *Initial oxygen absorption rates at* 79·7° *at different benzaldehyde concentrations.*



Initial rates of oxygen absorption in ml. of oxygen (at N.T.P.) per min. per mole of benzaldehyde. Chlorobenzene used as diluent. Initial concns. (in g./10 ml. of solution): [Ph·CO_2H] = 1·50; [Bz_2O_2] = 0·2400; [*m*-2-xylenol] = 0·0600.

the dependence on oxygen concentration is given by the relationship (3), where at atmospheric pressure the constant q is much smaller than $p[O_2]$:

$$-d[O_2]/dt = [O_2]/\{p[O_2] + q\} \quad . \ . \ . \ . \ . \ . \ . \quad (3)$$

Consequently, the retarded autoxidation of benzaldehyde solutions containing *m*-2-xylenol shows the same kinetic dependence on the concentration of the various components as does the similar system containing *p*-cresol. We infer, therefore, that *m*-2-xylenol, as such,

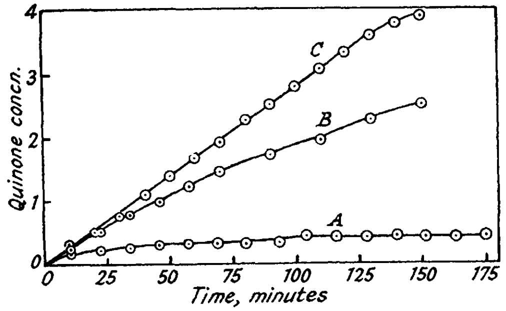
TABLE 1. *Effect of oxygen pressure on the autoxidation of benzaldehyde*–m-2-*xylenol mixtures at* 79·7°.

Initial concns., in g./10 ml. of Ph·CHO: Ph·CO$_2$H, 1·50; Bz$_2$O$_2$, 0·150; xylenol, 0·120. The initial oxygen uptake is measured in ml. of O$_2$ (at N.T.P.) min.$^{-1}$ mole^{-1} of Ph·CHO.

O$_2$ press., mm.	260·5	404·3	540	659·5	759
$-d[O_2]/dt$	5·58	5·83	6·25	6·10	6·25
$[O_2]/(-d[O_2]/dt)$ Found	46·5	69·5	86·5	108	121·5
$[O_2]/(-d[O_2]/dt)$ Calc. (p = 0·15, q = 8 mm.)	47	69	88	107	122

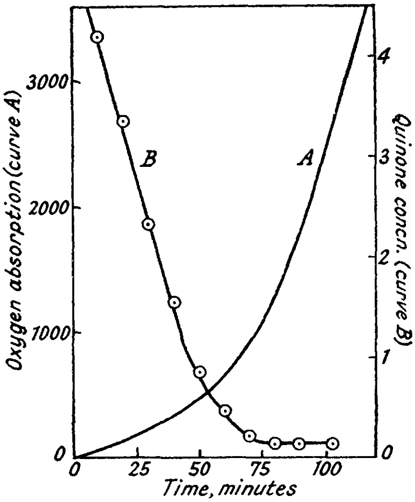
acts as a chain-transfer agent, and that the first chain-ending process mainly involves the interaction of a pair of (C$_8$H$_9$O•) radicals though there is a small, inexplicable, unimolecular destruction process (see Part I). It is unlikely that the latter is a surface reaction since added glass was without effect on the rate of the *p*-cresol-retarded autoxidation.

FIG. 4. *Formation of quinone during the oxidation of* m-2-*xylenol–benzaldehyde mixtures at* 79·7°.



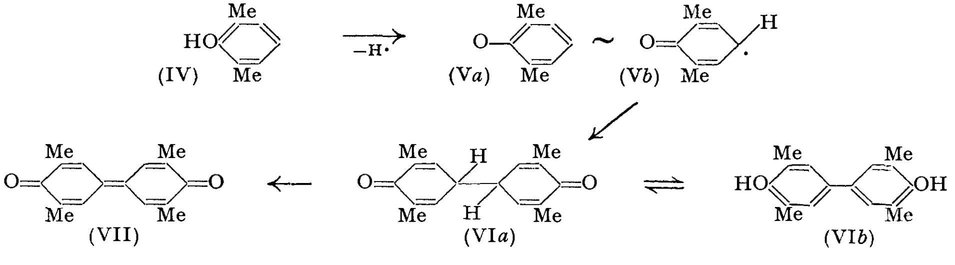
Quinone concns. in g./l. of solution. Initial concns. (in g./10 ml. of benzaldehyde): [Ph·CO$_2$H] = 1·50; [Bz$_2$O$_2$] = 0·1500; [*m*-2-xylenol]: Curve *A*, 0·0508; Curve *B*, 0·2540; Curve *C*, 0·5107.

FIG. 5. *Oxidation of a quinone–benzaldehyde mixture at* 79·7°.



Oxygen absorption in ml. of oxygen (at N.T.P.)/mole of benzaldehyde; quinone concn. in g./l. of solution. Initial concns. (in g./10 ml. of benzaldehyde): [Ph·CO$_2$H] = 1·50; [Bz$_2$O$_2$] = 0·1500; [quinone] = 0·0500. Curve *A*: course of oxygen absorption. Curve *B*: course of quinone destruction.

Now, the oxidised solutions of *m*-2-xylenol had become red, and from them we succeeded in isolating red 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone (VII) which would result if (VI), the expected dimer of the mesomeric radical (V), had been oxidised further by loss of a pair of hydrogen atoms.



The rate of formation of the diphenoquinone (VII) could be followed colorimetrically by using a " Spekker " photo-absorptiometer with a blue (No. 602) filter, and Fig. 4 shows the results obtained. From curve *A* of this graph it can be seen that when only a little xylenol is used then the amount of quinone formed fairly soon reaches a maximum, corresponding to about 10% conversion; oxygen uptake decreases somewhat initially, but eventually reaches a constant rate, corresponding to the maximum quinone concentration.

Curves *B* and *C* of Fig. 4 show that at high xylenol concentrations the initial rate of the diphenoquinone formation seems to approach a constant value. This was $2{\cdot}83 \times 10^{-2}$ g. per l. of solution per minute for a mixture containing initially 15 g. of benzoyl peroxide and 51·1 g. of *m*-2-xylenol per l. of benzaldehyde. The latter value may be compared with the rate of dimerisation of the ($C_8H_9O\cdot$) radical, ($= k_8[ArO\cdot]^2$).

From the kinetic relationships of Part I * it is found that

$$k_8[ArO\cdot]^2 = 2k_1\{([Bz_2O_2] + b)^{\frac{1}{2}} - c\}^2$$

where k_1 is the unimolecular velocity constant for the decomposition of benzoyl peroxide at 79·7°; *b* and *c* are constants indicative of other modes of chain initiation and termination (cf. Part I, p. 820), and may be evaluated from Fig. 2, the slope and *x*-axis intercept of curve *B* being used, together with the rate of oxygen absorption at zero benzoyl peroxide concentration given from curve *A*. Taking the value of k_1 at 80° as $2{\cdot}52 \times 10^{-3}$ min.$^{-1}$, as given by Swain, Stockmayer, and Clarke (*loc. cit.*), we obtain a computed value of $2{\cdot}5 \times 10^{-2}$ g. l.$^{-1}$ min.$^{-1}$ for the rate of dimerisation of the ($C_8H_9O\cdot$) radical. This is sufficiently close to the measured value for the rate of formation of the derived quinone for it to be inferred that the dimerisation process leads to a quantitative formation of 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone, and thereafter to colourless substances derived from it. However, owing to the uncertainty as to the true value for k_1 in autoxidising benzaldehyde (see p. 2426) and for the constants *b* and *c*, the foregoing deduction should be accepted with reserve.

The observations shown in Fig. 4, particularly in curve *A*, indicate that 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone is not the end product of the destruction of the *m*-2-xylenol by the autoxidising benzaldehyde. The quinone is, in fact, a powerful inhibitor of the autoxidation and is slowly destroyed thereby to give colourless or nearly colourless products which are very poor retarders of the autoxidation, for, as Fig. 5 (curve *A*) shows, the rate of oxygen absorption increases with time in benzaldehyde–benzoyl peroxide mixtures containing (VII).

When the initial autoxidation rates of mixtures containing (VII) were investigated, quite different kinetic relations from those appertaining to the benzaldehyde–*m*-2-xylenol system were observed (for details see Part III, following paper), the most significant being a *first-order* dependence on the concentration of the benzoyl peroxide catalyst, as is indicated by Table 2. Again, unlike both *p*-cresol and *m*-2-xylenol (compare Fig. 2), the 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone is a *complete* inhibitor of the autoxidation of benzaldehyde in the absence of benzoyl peroxide. As the kinetic analysis of the Table of Part I shows, this first-order dependence of the autoxidation rate upon benzoyl peroxide concentration indicates that the chain ending is achieved by combination of active radicals with the quinone, though it does not differentiate between a single-stage process (4) giving a stable semi-quinone RQ· and a two-stage process, (4) followed by (5), at a comparable rate:

$$(4)\quad R\cdot + Q \longrightarrow RQ\cdot \qquad (5)\quad RQ\cdot + R\cdot \longrightarrow R\text{–}Q\text{–}R$$

The kinetic theory also indicates that

$$n \times -d[\text{Quinone}]/dt = a \times -d[\text{Benzoyl peroxide}]/dt \quad . \quad . \quad . \quad (6)$$

where *a* is the number of reaction chains initiated by each molecule of benzoyl peroxide, and has the ***maximum*** value of *two*, as indicated by equation (7), whilst *n* is the number of

$$Ph{\cdot}CO{\cdot}O\text{—}O{\cdot}CO{\cdot}Ph \xrightarrow{k_1} 2Ph{\cdot}CO{\cdot}O\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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* In deriving the theoretical equations of Part I an error was made in giving the rate of formation of $Ph{\cdot}CO_2\cdot$ radicals as $\frac{1}{2}k_1[Bz_2O_2]$; it should be, as above, $2k_1[Bz_2O_2]$.

reaction chains terminated by each quinone molecule; *n* has the probable value of *two* also if, as indicated by the work of Bickel and Waters (*J.*, 1950, 1764), combination of radicals occurs at both oxygen atoms of the quinone. The value of *one* for *n* is impossible unless the semiquinone radical RQ· is *completely* stable, for a stabilising process such as (8), following (4), corresponds to chain transfer and not to chain termination.

TABLE 2. *Effect of benzoyl peroxide concentration on the initial rate of oxygen uptake in the presence of* 3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*diphenoquinone.*

O_2 absorption is measured in ml. of O_2 (at N.T.P.) min.$^{-1}$ mol.$^{-1}$ of Ph·CHO. Temp. 79·7°. Initial concns. (g./10 ml. Ph·CHO): Ph·CO$_2$H, 1·50; quinone, 0·0300.

Peroxide, g./10 ml.	0·031	0·060	0·090	0·121	0·122	0·150	0·150	0·180	0·239	0·268	0·300
Rate	2·8	5·0	7·6	7·9	9·4	12·1	13·1	13·2	17·5	20·5	23·4
Rate/Peroxide	90	83	86	64	78	80	87	74	73	77	78
											Mean 79·1

TABLE 3. *Rate of destruction of* 3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*diphenoquinone by autoxidising benzaldehyde.*

(Each solution contained 3·00 g. of benzoic acid and 0·225 g. of benzoyl peroxide in 20 ml. of benzaldehyde.)

Initial quinone concn. (g. l.$^{-1}$)	2·50	3·75	5·00	6·25	7·50	9·00
Initial rate of quinone destruction (g. l.$^{-1}$ min.$^{-1}$) × 10^2	4·81	5·25	4·97	5·12	4·98	5·26
						Mean 5·06 ± 0·2

$$\mathrm{RQ\cdot + Ph\cdot CHO \longrightarrow R{-}Q{-}H + Ph\cdot CO\cdot} \qquad . \ . \ . \ . \ (8)$$

Equation (6) indicates that the rate of destruction of the quinone should depend only on the rate of decomposition of the benzoyl peroxide. When a sufficient excess of benzoyl peroxide was taken, the rate of destruction of (VII) was found to be a zero-order process for at least 50% of its decomposition, as curve B of Fig. 5 shows. Table 3 also verifies that the initial rate is independent of the initial quinone concentration.

TABLE 4. *Initial rates of quinone destruction at* 79·7° *at different benzoyl peroxide concentrations.*

[Initial concns. (in g./10 ml. of Ph·CHO): Ph·CO$_2$H, 1·50; quinone, 0·050; $-\,dQ/dt$ is measured in g. of quinone per l. of solution per min.]

Peroxide (g./10 ml.)	0·225	0·188	0·169	0·150	0·131	0·112	0·0812	0·0650	0·0650	0·0500
$-\,dQ/dt$	11·25	9·28	8·42	7·43	6·60	5·95	4·40	3·80	4·10	3·22
$-\,dQ/dt$/[Peroxide]	5·00	4·96	5·00	4·96	5·02	5·28	5·42	5·84	6·30	6·44

TABLE 5. *Rates of destruction of* 3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*diphenoquinone under different conditions.*

(Each solution contained 3·00 g. of benzoic acid, 0·225 g. of benzoyl peroxide, and 0·100 g. of quinone in 20 ml. of solvent.)

Conditions	Initial decomp. rate
Benzaldehyde solution with O_2 passing	5·0 × 10^{-2} g. l.$^{-1}$ min.$^{-1}$
Benzaldehyde solution with N_2 passing	3·2 × 10^{-2} ,,
Chlorobenzene solution	1·3 × 10^{-2} ,,

TABLE 6. *Initial rates of quinone destruction at* 79·7° *at different concentrations of benzaldehyde in chlorobenzene.*

Initial concns. (in g./10 ml. of solution) at room temperature: Ph·CO$_2$H, 1·50; quinone, 0·050; (Ph·CO·O)$_2$, 0·1125.

(Allowance has been made for the change in absolute concentration of the benzoyl peroxide owing to the expansion of the mixtures on heating to 79·7°. The initial rates of quinone destruction are given in 10^{-2} g. l.$^{-1}$ min.$^{-1}$.)

Benzaldehyde, %	100	75	50	25	10	0
$-\,d[\text{Quinone}]/dt$ [Benzoyl peroxide]	5·02	5·04	5·28	4·40	3·00	1·30

Table 4 shows that when the quinone concentration is kept constant the initial rate at which it is destroyed is proportional to the benzoyl peroxide concentration until low values of the latter are reached. If every free radical produced by the decomposition of the benzoyl peroxide were eventually converted into radicals which combined with the quinone then solvents, or oxygen, should not affect the rate of its disappearance. This does not seem to be the case, as Table 5 shows, though Table 6 shows that under autoxidation conditions dilution of the benzaldehyde with as much as 50% of chlorobenzene has no significant effect upon the rate of destruction of the quinone. It appears, therefore, that under autoxidation conditions in benzaldehyde solution nearly every free radical produced by the decomposition of the benzoyl peroxide does lead to a reaction chain which is terminated eventually by radical capture by the quinone, though in the absence of oxygen, and more especially in the inert solvent chlorobenzene this condition may not hold.

The work of Swain, Stockmayer, and Clarke (*loc. cit.*) indicated that under conditions of radical capture by polymerisable olefins the true unimolecular rate of decomposition of benzoyl peroxide at 80° in dioxan tended to a lower limit of $k_1 = 2{\cdot}52 \times 10^{-3}$ min.$^{-1}$. Earlier, Nozaki and Bartlett (*J. Amer. Chem. Soc.*, 1946, **68**, 1686) had given a range of values at 79·8° of $1{\cdot}16$—$5{\cdot}38 \times 10^{-3}$ min.$^{-1}$ for different solvents, with a constant value of $1{\cdot}97 \times 10^{-3}$ min.$^{-1}$ in benzene, toluene, and nitrobenzene. Quite recently, however, Bawn and Mellish (*Trans. Faraday Soc.*, 1951, **47**, 1216), who like ourselves have used a colorimetric method depending upon radical capture, have shown that the rate of decomposition of benzoyl peroxide is in fact solvent-dependent though the activation energy of the decomposition process remains constant at the value of 29·6 kcal. Now from the slope of the linear portion of the curve based on the data of Table 4 we find that $-\mathrm{d}Q/\mathrm{d}t/[\text{Benzoyl peroxide}] = 5{\cdot}8 \times 10^{-3}$ min.$^{-1}$. From equation (6), $-\mathrm{d}[\text{Quinone}]\mathrm{d}t/(-\mathrm{d}[\text{Benzoyl peroxide}]/\mathrm{d}t) = a/n$. On putting $-\mathrm{d}[\text{Benzoyl peroxide}]/\mathrm{d}t = k_1[\text{Benzoyl peroxide}]$, we get $\mathrm{d}[\text{Quinone}]/\mathrm{d}t/[\text{Benzoyl peroxide}] = (a/n) \,.\, k_1$. Hence, if we assume that $a = n = 2$ then the rate of decomposition of benzoyl peroxide in benzaldehyde solution containing oxygen is comparable with the highest value given by Nozaki and Bartlett, though the data given in Table 5 may indicate that it becomes decidedly less in the absence of oxygen or in chlorobenzene solution.

EXPERIMENTAL

Oxygen-uptake Measurements.—The purification of materials, and the oxygen-uptake measurements were carried out by the procedure described in Part I, the larger quantities of inhibitor being weighed into the reaction flasks direct, rather than being used as a solution in benzaldehyde. At 79·7°, the water-thermostat was controlled to ±0·1°, and the preliminary evacuation reduced to 45 seconds without shaking (when chlorobenzene was present, it was necessary to fill and evacuate the reaction vessel in the cold). In all cases, the initial rate of reaction was computed as the average rate of oxygen absorption over the first 10·5 minutes, and again it was found that the experimental results of two operators (Mrs. A. M. B. and C. W.-J.), using independent apparatus, could be combined.

Determination of Quinone Concentrations.—The results of Fig. 4 (Curves *B* and *C*) and of Tables 3, 4, and 5 were obtained by extracting 1-ml. samples at suitable time intervals from reaction mixtures, through which oxygen was slowly bubbled—these measurements were concordant with those obtained when the oxygen absorption was simultaneously determined, as was the case for Figs. 4 (*A*) and 5. The latter samples were diluted to 100 ml. with xylene, and their quinone contents compared colorimetrically, a "Spekker" photoelectric absorptiometer with blue filters (No. 602) being used. Absolute values were obtained by reference to a calibration curve constructed by the use of a standard quinone solution (0·0500 g./l. of xylene), which had to be stored in the dark to prevent loss of colour intensity. The latter curve was quite reproducible, though to ensure the reliability of the instrument, at least two points were independently re-checked every day. In order to obtain constancy, all "Spekker" readings had to be performed in the dark.

Isolation of Products from the Benzaldehyde–m-2-*Xylenol System.*—Combined products from several kinetic experiments, containing in all 9 g. of benzoic acid, 0·9 g. of benzoyl peroxide, and 0·7 g. of *m*-2-xylenol in 60 ml. of benzaldehyde were distilled in steam, after the removal of benzoic acid with aqueous sodium hydrogen carbonate. The aqueous residue contained a red powder insoluble in ether. This was crystallised from glacial acetic acid, and proved to be identical with an authentic specimen of 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diphenoquinone (Cosgrove and Waters, *loc. cit.*, 1951) by m. p. and mixed m. p. 190° (decomp.). The further examination of products of this reaction is reported in Part IV (*J.*, 1952, 2432).

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