

178. The Retardation of Benzaldehyde Autoxidation by *p*-Cresol.

By WILLIAM A. WATERS and CHARLES WICKHAM-JONES.

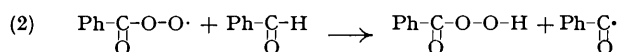
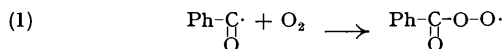
A kinetic study has been made of the effect of *p*-cresol on the benzoyl peroxide-catalysed autoxidation of benzaldehyde. The decomposition of perbenzoic acid by a first-order acid-base-catalysed process tends to complicate the reaction kinetics of the early stages of the autoxidation. This effect can be controlled by the initial addition of sufficient benzoic acid. In these circumstances, the rate of autoxidation is (a) approximately proportional to the square root of the benzoyl peroxide concentration, (b) proportional to the square of the benzaldehyde concentration, (c) inversely proportional to the *p*-cresol concentration, and (d) nearly independent of the oxygen concentration. These results can be accounted for by postulating that *p*-cresol acts in the main as a chain transfer agent, and that chain termination involves the destruction of *p*-tolyl radicals principally by dimersation.

This paper deals with a kinetic approach to the general problem of the mode of action of monohydric phenols in retarding, or inhibiting, the autoxidation of organic liquids. *p*-Cresol has been selected for this study because a considerable amount of information concerning the way in which it undergoes oxidation when treated with free-radical producing agents has recently been accumulated in this laboratory (Cosgrove and Waters, *J.*, 1949, 3189). Benzaldehyde was chosen as the autoxidisable substrate chiefly because it absorbs oxygen so easily at moderate temperatures to give almost exclusively the known products, benzoic acid and perbenzoic acid. However, it now appears that aldehydes are by no means ideal substrates for autoxidation studies, since the oxidation process as a whole is seriously complicated by the ease of decomposition of the initially-formed per-acids. Fortunately, with perbenzoic acid, this decomposition is in the main an acid-base-catalysed process (cf. Wittig and Pieper, *Annalen*, 1941, 546, 142) which can be controlled by adding a sufficient amount of benzoic acid initially to the reacting system (see p. 816).

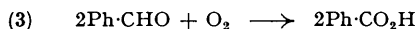
The initiation of the autoxidation of all reasonably well-purified organic substances is probably to be ascribed to residual traces of catalytically active impurities in the substance itself or on the walls of the reaction vessel. Consequently, the autoxidation of "purified" benzaldehyde is a rather erratic process at the outset, some workers even claiming that highly purified benzaldehyde does not autoxidise (see Bailey, "The Retardation of Chemical Reactions," Arnold, London, 1937, Chap. 11). Our own early measurements showed large rate variations from run to run, but they became much more reproducible when the decomposition of the perbenzoic acid was controlled as mentioned above. Eventually we obtained consistent results by this means and by also swamping the action of the adventitious catalysts by adding known amounts of benzoyl peroxide so as to provide a regular source of active free benzoate radicals for initiating autoxidation chains, and thereafter we were able to elucidate the modes of action of *p*-cresol as a retarding agent. The outcome of this work is considered in the following sections.

(I) *The Role of Perbenzoic Acid.*

It was established by Bäckström (*J. Amer. Chem. Soc.*, 1927, 49, 1460) that the uptake of oxygen by benzaldehyde is essentially a chain reaction, whose propagation steps we may now represent by equations (1) and (2). This cycle yields perbenzoic acid as the initial reaction product, but



the latter soon breaks down so that, when the autoxidation of benzaldehyde has proceeded for some time, benzoic acid accumulates at a rate almost identical with that of oxygen uptake (Almquist and Branch, *J. Amer. Chem. Soc.*, 1932, 54, 2293) and thereafter the reaction apparently becomes simple as in equation (3).



In the absence of added catalysts, or inhibitors, the rapid autoxidation of benzaldehyde does appear to slacken according to the second-order relationship

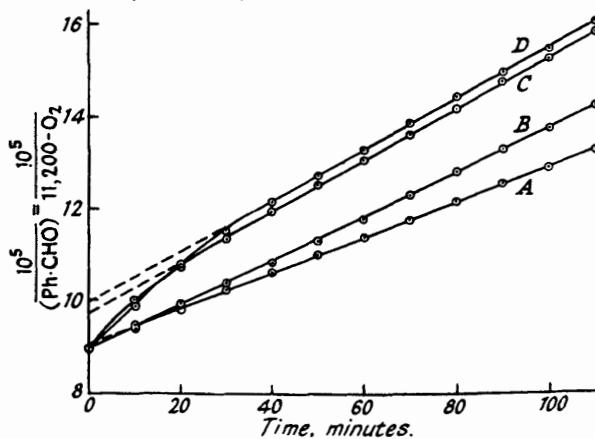
$$-d[\frac{1}{2}O_2]/dt = -d[Ph\cdot CHO]/dt = k \cdot [Ph\cdot CHO]^2$$

since Fig. 1, in which  $\Delta[Ph\cdot CHO]$  has been computed in terms of the total oxygen uptake, shows that the integrated expression for a second-order reaction

$$1/[Ph\cdot CHO] = kt + \text{constant}$$

does hold for quite a considerable time interval both for benzaldehyde alone and for mixtures with the inert diluent chlorobenzene.

FIG. 1  
Oxidation of benzaldehyde-chlorobenzene mixtures at 20.0°.



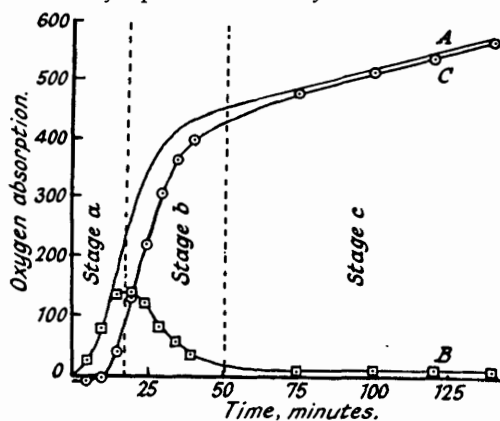
Curves A & B : 100% Benzaldehyde.

Curve C : 50% Benzaldehyde + 50% chlorobenzene.

Curve D : 20% Benzaldehyde + 80% chlorobenzene.

[ $O_2$  = oxygen absorbed (in ml. at N.T.P. per mole of benzaldehyde).]

FIG. 2.  
Oxidation of a *p*-cresol-benzaldehyde mixture at 30.0°.



Concentration of *p*-cresol = 0.00053 g./10 ml. of benzaldehyde.

Curve A : Oxygen absorption (ml. of  $O_2$  at N.T.P./mole of benzaldehyde).

Curve B : Peroxide values

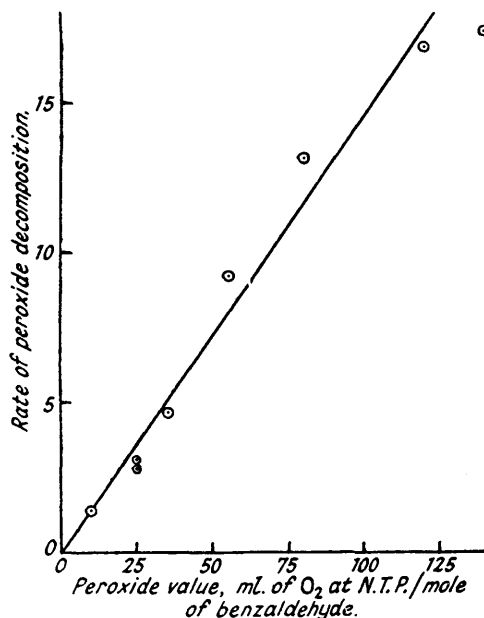
Curve C : Peroxide decomposition values } calculated as equivalents of the oxygen absorbed.

In the chosen circumstances, the initial phase of the autoxidation occurred too rapidly for investigation. Fig. 2, however, which gives a typical autoxidation curve for benzaldehyde containing a very small amount of *p*-cresol, shows that the reaction includes both an initial,

brief, autocatalytic stage *a* in which the rate of oxygen uptake (see curve *A*) increases with time, and a subsequent stage *b* of autoxidation at diminishing rate, which is finally succeeded by a prolonged stage *c* of slowish but almost constant rate of reaction. The titratable peroxide content of the liquid (see curve *B*) rises in stage *a* to a maximum, approximately coincident with the moment of fastest oxygen uptake, and then falls off during stage *b* to a low but steady value, which remains almost constant in stage *c*. It may be noted that the rate of peroxide decomposition, which may be plotted from the measurements of (oxygen uptake) — (peroxide value) (see curve *C*), increases with time, and, at identical peroxide concentrations, is very much faster after the peroxide has attained its peak value (stage *b*) than before it (stage *a*).

FIG. 3.

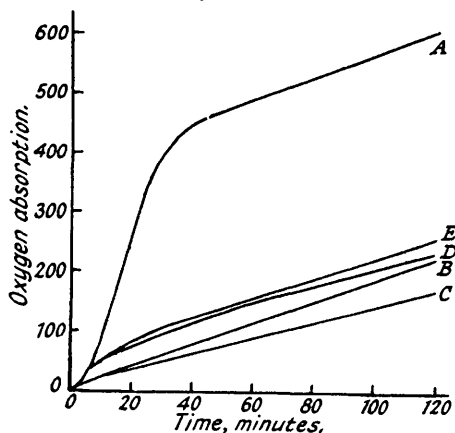
Decomposition of peroxide during the oxidation of a *p*-cresol-benzaldehyde mixture at 30.0°.



Rate of peroxide decomposition in ml. of O<sub>2</sub> (at N.T.P.)/min./mole of benzaldehyde.  
Concentration of *p*-cresol = 0.00053 g./10 ml. of benzaldehyde.  
Results calculated from data of Fig. 2.

FIG. 4.

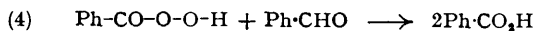
Effect of acids and bases on the oxidation of a *p*-cresol-benzaldehyde mixture at 30.0°.



Oxygen absorption in ml. of oxygen (at N.T.P.)/mole of benzaldehyde.  
Concentration of *p*-cresol = 0.00106 g./10 ml. of benzaldehyde.  
Initial addition of acid or base (to 10 ml. of benzaldehyde):

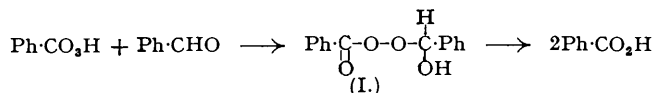
- Curve A: none.
- Curve B: 0.55 g. of benzoic acid (0.0455 mole/mole benzaldehyde).
- Curve C: 0.21 g. of trichloroacetic acid (0.013 mole/mole benzaldehyde).
- Curve D: 0.5 ml. of pyridine (0.0625 mole/mole benzaldehyde).
- Curve E: 0.48 g. of anhydrous potassium carbonate (0.035 mole/mole benzaldehyde).

Fig. 3, obtained by correlating the slope of curve *C* in stages *b* and *c* of Fig. 2 with the corresponding peroxide value given in curve *B*, indicates that the rate of perbenzoic acid decomposition is a first-order process once the peak value has been passed. This substantiates Wittig and Pieper's findings (*loc. cit.*) for benzaldehyde-carbon tetrachloride mixtures and accords with the simple equation (4) originally proposed by Baeyer and Villiger (*Ber.*, 1900, **33**, 1569).



Almqvist and Branch (*loc. cit.*) were the first workers to discover that the peroxide content of autoxidising benzaldehyde passed through a peak value. They showed that this peak was not exhibited by samples of benzaldehyde to which benzoic acid had been added initially, and that the peroxide content of such mixtures quickly rose to a steady value. Their interpretation of this phenomenon involved the postulation of the existence of both active and inactive forms of the peroxide. Wittig and Pieper have, more correctly, ascribed the effect of benzoic acid upon the rate of decomposition of perbenzoic acid to acid catalysis of the Baeyer and Villiger reaction (4). They suggested that the benzoic acid catalyses an acetal-like addition of perbenzoic

acid to benzaldehyde to yield a complex (I) which rapidly breaks down into **two benzoic acid** molecules :



We have confirmed this work, and in addition have shown that other acids, *e.g.*, trichloroacetic acid, and bases, *e.g.*, pyridine and anhydrous potassium carbonate, have a similar effect (see Fig. 4). We therefore suggest that the formation of the benzaldehyde-perbenzoic acid complex (I) is an acid-base-catalysed reaction, typical of a carbonyl addition process, and proceeds thus :

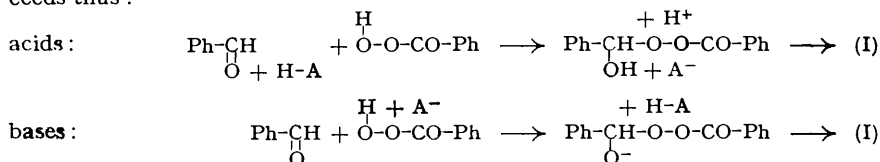
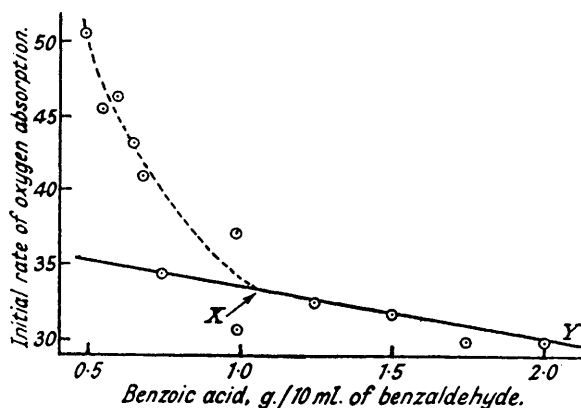


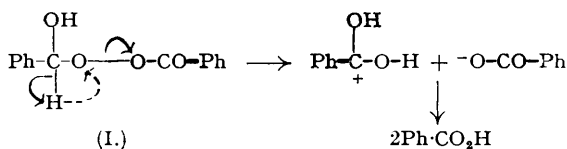
FIG. 5.

Initial oxygen absorption rates at 40.0° at different benzoic acid concentrations.



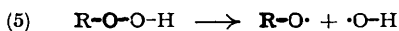
Rate in ml. of oxygen (at N.T.P.) per min. per mole of benzaldehyde.  
 $[\text{Bz}_2\text{O}_2] = 0.2000 \text{ g./10 ml. of benzaldehyde.}$   
 $[\text{p-C}_6\text{H}_4\text{Me}\cdot\text{OH}] = 0.000424 \text{ g./10 ml. of benzaldehyde.}$

The decomposition of the complex (I) can follow the ionic scheme suggested by Robertson and Waters (*J.*, 1948, 1574) for the reaction of Caro's acid with ketones :



This involves the migration of hydrogen as an anionoid group from carbon to an adjoining oxygen atom so as to effect the oxidation of the benzaldehyde moiety.

This acid-base-catalysed reaction between perbenzoic acid and benzaldehyde cannot, however, be the only type of decomposition which perbenzoic acid can undergo, for, in all stages of the autoxidation, changes in the oxygen-uptake rate are associated with changes in the peroxide content of the aldehyde (see Fig. 2), just as is found in the autoxidation of tetralin (Robertson and Waters, *J.*, 1948, 1585), ethyl linoleate (Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 236), and similar substances. In these latter cases, the acceleration of the autoxidation rates has been ascribed to the production of additional chain-starting radicals by the homolytic peroxide decomposition (5).

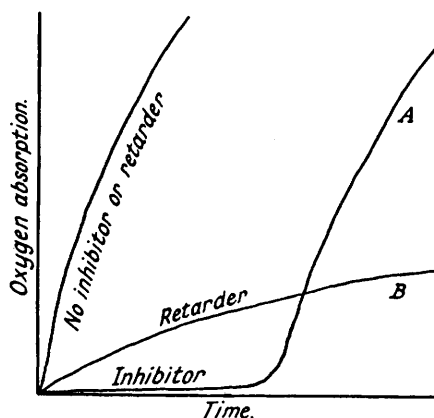


The ionic reactions of perbenzoic acid described above would not produce fragments capable of initiating fresh autoxidation chains. We would therefore suggest that some slight homolytic decomposition also occurs to give small traces of  $\text{Ph}\cdot\text{CO}_2\cdot$  and  $\cdot\text{OH}$  radicals, both of which would be autoxidation chain initiators. In this way the form of curve *A* in Fig. 2 can be qualitatively accounted for, since a reaction of type (5) would occur increasingly as the peroxide content of the reaction mixture rises (stage *a*), but will become very slight again as the peroxide content decreases (stage *b*) owing to the onset of the acid-catalysed decomposition.

If we add a sufficient quantity of acid or base initially to the benzaldehyde-*p*-cresol system, we can cut out stages *a* and *b* of Fig. 2 and proceed at once with the steady state of stage *c* (see Fig. 4). Fig. 5 shows the effect of benzoic acid on the initial rate of oxygen uptake for a mixture containing both *p*-cresol and benzoyl peroxide. At a benzoic acid concentration corresponding to point *X*, the equilibrium concentration of perbenzoic acid is rapidly reached; further addition of benzoic acid serves only to dilute the reacting liquid, and the subsequent decrease in the initial oxygen-uptake rate is approximately the same as that which would be achieved by adding a corresponding molar fraction of an inert diluent (the slope of the line *XY* in Fig. 5 is that calculated for the addition to the mixture of an inert diluent of molecular weight 122). In the kinetic investigations (Section II), we have always added initially a greater

FIG. 6.

Typical effects of inhibitors and retarders on autoxidation systems.



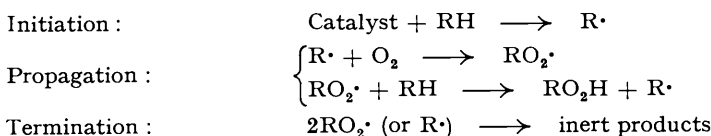
amount of benzoic acid than is indicated by point *X* in Fig. 5 (in the majority of cases, this was 1.50 g./10 ml. of benzaldehyde; in the remainder, the amount varied and the experimental value of the oxygen-uptake rate was corrected for this variation).

### (II) The Kinetics of the Retarded Autoxidation.

The significant feature of the autoxidation of benzaldehyde in the presence of *p*-cresol is the fact that oxygen uptake proceeds at a slow but yet steady rate for a long time. Even when the oxidising liquid has taken up several hundred moles of oxygen per mole of *p*-cresol, the rate-controlling action of the latter is still operative. Hence *p*-cresol must act in a different way from those inhibitors of autoxidation which are slowly consumed during an "induction period" of very slow oxidation, and thereafter exert no decided check on the reaction velocity—*e.g.*, many unsaturated hydrocarbons (Wittig and Pieper, *Annalen*, 1947, 558, 207) and anthracene (Branch, Almqvist, and Goldsworthy, *J. Amer. Chem. Soc.*, 1933, 55, 4052). These inhibitors give an autoxidation curve of type *A* (see Fig. 6) and their destruction during the induction period has in certain instances been demonstrated by physical and chemical tests (Wittig and Pieper, *loc. cit.*, 1947; Bäckström and Beatty, *J. Physical Chem.*, 1931, 35, 2530; Aleya and Bäckström, *J. Amer. Chem. Soc.*, 1929, 51, 90). The much greater persistence of a retarder such as *p*-cresol, however (which gives an autoxidation curve of type *B* in Fig. 6), may be inferred from the very long time in which it operates (as compared with the action of inhibitors of the former type). Indeed, the slow autoxidation of *n*-butaldehyde containing a little *p*-cresol has been carried out until over 90% of the aldehyde has been oxidised to butyric acid, and yet in the

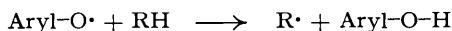
resulting product over 60% of the *p*-cresol has been found still to be present (private communication from Dr. D. G. Jones, Imperial Chemical Industries Limited, Billingham).

It therefore follows that in an autoxidation process of the usual chain type



the role of *p*-cresol cannot be only the removal of active radicals ( $\text{R}\cdot$ ,  $\text{RO}_2\cdot$ , etc.) or of catalyst, as is the case for inhibitors giving curves of type *A* (Fig. 6), but must also be that of a retarding agent which hinders the main oxidation chain by chemical reactions in which it is re-formed. Such a role is possible only with a *chain transfer agent* which substitutes a sequence of slow reactions for a sequence of rapid ones.

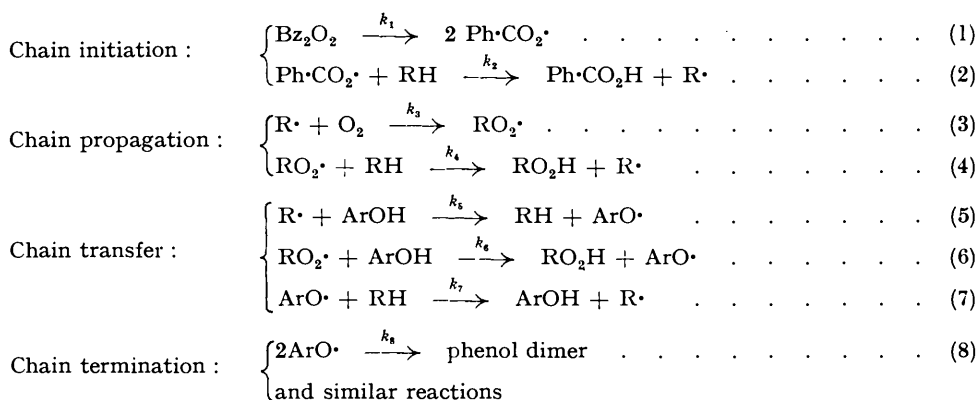
The chemical properties of phenols are such as to permit them to act as chain transfer agents in reactions involving homolytic dehydrogenation, since the removal of a hydrogen atom from a monohydric phenol ( $\text{Aryl-O-H}$ ) yields a mesomeric semi-quinol radical ( $\text{Aryl-O}\cdot$ ) which is much more stable than a free alkyl or aryl radical, but much less stable than the semi-quinone radical ion ( $\cdot\text{O}-\text{C}_6\text{H}_4-\text{O}\cdot$ ) of a 1:2- or 1:4-dihydric phenol. Consequently, one can reasonably postulate that the semi-quinol radical of a monohydric phenol may be capable of dehydrogenating easily autoxidisable substrates thus (cf. Cosgrove and Waters, *J.*, in the press) :



Bolland and ten Have (*Disc. Faraday Soc.*, 1947, **2**, 252) have tentatively suggested that this may be possible, but could adduce no evidence for it from their own work. Bickel and Waters (*J.*, 1950, 1764), however, have already found some experimental evidence of a similar process in reactions associated with vinyl polymerisation.

Normally the ( $\text{Aryl-O}\cdot$ ) radicals will tend to accumulate, and, as the study of their organic chemistry has shown in this laboratory, they can eventually combine with each other to form complex phenol dimers; again we have found no evidence of their reaction with free oxygen.

Thus a retarded autoxidation involving chain transfer can be represented by the following reaction sequence :



where  $\text{Bz}_2\text{O}_2$  denotes chain-initiating catalyst (benzoyl peroxide),  $\text{RH}$  denotes substrate (benzaldehyde), and  $\text{ArOH}$  denotes retarder (*p*-cresol).

By taking reactions (1)–(8) only, and by considering the stationary states (i)  $d[\text{Ph}\cdot\text{CO}_2\cdot]/dt = 0$ , (ii)  $d[\text{ArO}\cdot]/dt = 0$ , (iii)  $d[\text{R}\cdot]/dt = 0$ , and (iv)  $d[\text{RO}_2\cdot]/dt = 0$ , we have the equations

$$\begin{array}{l} \text{(i)} \quad \frac{1}{2}k_1[\text{Bz}_2\text{O}_2] = k_2[\text{RH}][\text{Ph}\cdot\text{CO}_2\cdot] \\ \text{(ii)} \quad k_5[\text{Ar}\cdot\text{OH}][\text{R}\cdot] + k_6[\text{Ar}\cdot\text{OH}][\text{RO}_2\cdot] = k_7[\text{RH}][\text{ArO}\cdot] + k_8[\text{ArO}\cdot]^2 \\ \text{(iii)} \quad k_2[\text{RH}][\text{Ph}\cdot\text{CO}_2\cdot] + k_4[\text{RH}][\text{RO}_2\cdot] + k_7[\text{RH}][\text{ArO}\cdot] = k_3[\text{O}_2][\text{R}\cdot] + k_5[\text{Ar}\cdot\text{OH}][\text{R}\cdot] \\ \text{(iv)} \quad k_3[\text{O}_2][\text{R}\cdot] = k_4[\text{RH}][\text{RO}_2\cdot] + k_6[\text{Ar}\cdot\text{OH}][\text{RO}_2\cdot] \end{array}$$

Adding (i), (ii), (iii), and (iv), we have

$$\frac{1}{2}k_1[\text{Bz}_2\text{O}_2] = k_8[\text{ArO}\cdot]^2$$

so that

$$[\text{ArO}\cdot] = \{k_1[\text{Bz}_2\text{O}_2]/2k_8\}^{\frac{1}{2}}$$

From (ii)

$$[\text{RO}_2\cdot] = \frac{k_7[\text{RH}][\text{ArO}\cdot] + k_8[\text{ArO}\cdot]^2 - k_8[\text{Ar}\cdot\text{OH}][\text{R}\cdot]}{k_6[\text{Ar}\cdot\text{OH}]}$$

Substituting this in (iv), we have

$$k_3[\text{O}_2][\text{R}\cdot]k_6[\text{Ar}\cdot\text{OH}] = \{k_4[\text{RH}] + k_6[\text{Ar}\cdot\text{OH}]\}\{k_7[\text{RH}][\text{ArO}\cdot] + k_8[\text{ArO}\cdot]^2 - k_8[\text{Ar}\cdot\text{OH}][\text{R}\cdot]\}$$

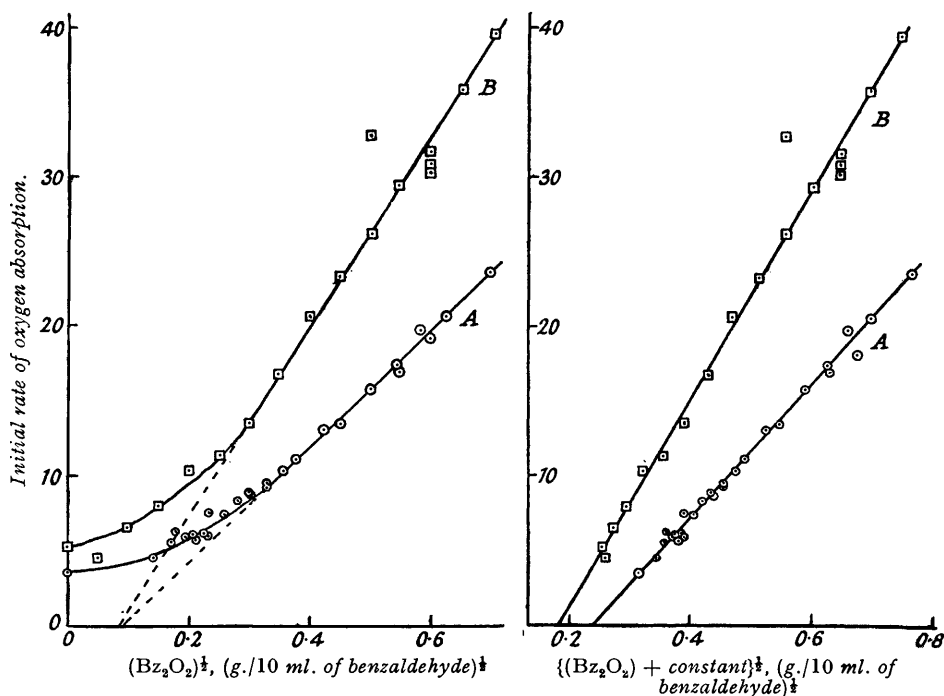
whence

$$-d[\text{O}_2]/dt = k_3[\text{O}_2][\text{R}\cdot] \\ = \frac{k_3[\text{O}_2]\{k_4[\text{RH}] + k_6[\text{Ar}\cdot\text{OH}]\}\left\{k_7[\text{RH}]\left(\frac{k_1}{2k_8}[\text{Bz}_2\text{O}_2]\right)^{\frac{1}{2}} + \frac{k_1}{2}[\text{Bz}_2\text{O}_2]\right\}}{[\text{Ar}\cdot\text{OH}]\{k_3k_6[\text{O}_2] + k_4k_6[\text{RH}] + k_8k_6[\text{Ar}\cdot\text{OH}]\}}$$

FIG. 7.

FIG. 8.

Initial oxygen absorption rates at 40.0° at different benzoyl peroxide concentrations.



Rates of absorption in ml. of oxygen (at N.T.P.)/min./mole benzaldehyde.  
 Curve A:  $[p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OH}] = 0.00106$  g./10 ml. of benzaldehyde.  
 Rates corrected to  $[\text{Ph}\cdot\text{CO}_2\text{H}] = 1.50$  g./10 ml. of benzaldehyde.  
 Curve B:  $[p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OH}] = 0.000636$  g./10 ml. of benzaldehyde.  
 $[\text{Ph}\cdot\text{CO}_2\text{H}] = 1.50$  g./10 ml. of benzaldehyde.

An examination of the reaction sequence (1)—(8) suggests that at small retarder concentrations: (a) Reaction (4) will probably be much faster than reaction (6) since  $[\text{RH}] \gg [\text{Ar}\cdot\text{OH}]$ ; hence, as an approximation we can put  $k_4[\text{RH}] \gg k_6[\text{Ar}\cdot\text{OH}]$ . (b) Reaction (7) may well be much faster than reaction (8) since  $[\text{RH}] \gg [\text{ArO}\cdot]$ , and one knows that the homolytic dehydrogenation of aldehydes is a very easy process. If this is so, we can make the approximation  $k_7[\text{RH}] \gg k_8[\text{ArO}\cdot] = \left\{\frac{1}{2}k_1k_8[\text{Bz}_2\text{O}_2]\right\}^{\frac{1}{2}}$ .

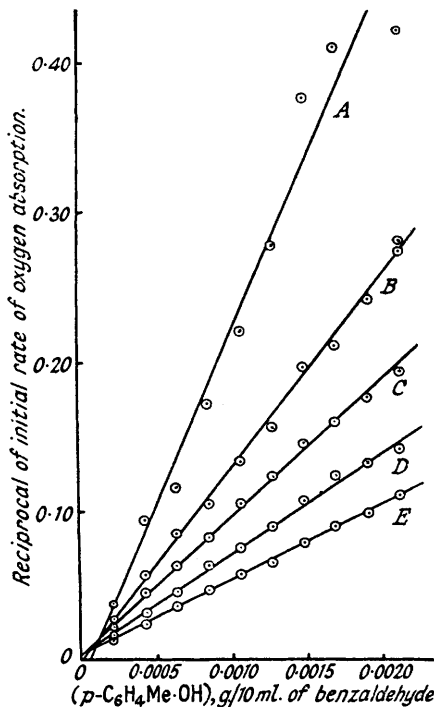
With these two approximations, we obtain the kinetic relationship (A)

$$-d[O_2]/dt = \frac{k_3 k_4 k_7 [O_2] [RH]^2 \left\{ \frac{k_1}{2k_8} [Bz_2O_2] \right\}^{\frac{1}{2}}}{[Ar\cdot OH] \{ k_3 k_6 [O_2] + k_4 k_5 [RH] \}} \dots \dots \dots (A)$$

which is in better accord with our experimental findings than the equations which can be deduced from alternative postulates (see Table, p. 822).

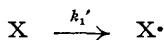
Fig. 7 shows that the rate of autoxidation of a benzaldehyde-*p*-cresol mixture is approximately proportional to the half power of the benzoyl peroxide concentration at large values of the latter only, but the extrapolation of this linear plot does not pass through the origin. At zero benzoyl peroxide concentration, there is still an appreciable oxidation rate, so benzoyl peroxide is not the only chain-initiating catalyst present in the system.

FIG. 9.  
Initial oxygen absorption rates at 40.0° at different *p*-cresol concentrations.

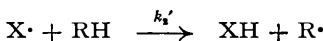


Rates of absorption in ml. of oxygen (at N.T.P.)/min./mole of benzaldehyde.  
Benzoyl peroxide concentrations (g./10 ml. of benzaldehyde) : Curve A, 0.0200; Curve B, 0.0543  
Curve C, 0.1086; Curve D, 0.2000; Curve E, 0.3000.  
Rates corrected to [Ph·CO<sub>2</sub>H] = 1.50 g./10 ml. of benzaldehyde in each case except curve D where no correction was necessary.

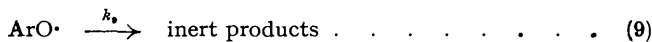
These features of Fig. 7 may be satisfactorily accounted for by suggesting : (i) an additional chain initiation



followed by



where X possibly represents that fraction of the decomposition of perbenzoic acid which is chain starting (see Section I, p. 815); (ii) an additional unimolecular chain-termination reaction (9) as well as the bimolecular reaction (8). It is difficult to picture the organic chemistry of such a radical destruction as reaction (9), unless it is perhaps a surface reaction.





The postulation of these additional reactions will modify the term  $\{k_1[\text{Bz}_2\text{O}_2]/2k_8\}^{\frac{1}{2}}$  in equation (A) to the more complex form

$$\sqrt{\frac{k_1}{2k_8}} \sqrt{[\text{Bz}_2\text{O}_2] + \frac{2k_1'}{k_1} [\text{X}] + \frac{k_9^2}{2k_1k_8}} - \frac{k_9}{\sqrt{2k_1k_8}}$$

whilst the terms involving  $[\text{RH}]$ ,  $[\text{O}_2]$ , and  $[\text{Ar}\cdot\text{OH}]$  are unaltered.

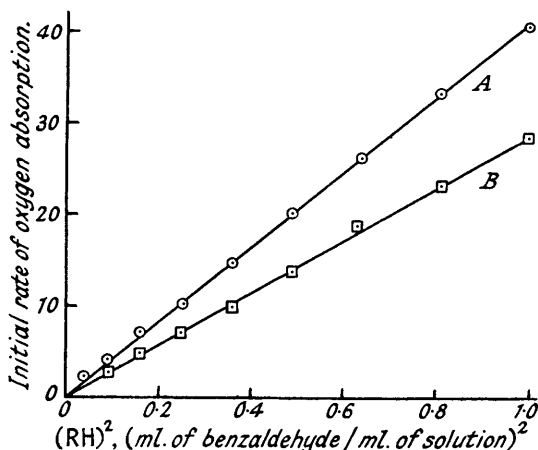
From the experimental data of Fig. 7, it is possible to derive, by the method of successive approximations, a linear relation of the form

$$d[\text{O}_2]/dt = a\{\sqrt{[\text{Bz}_2\text{O}_2] + b} - c\}$$

for all concentrations of  $[\text{Bz}_2\text{O}_2]$ , which is shown in Fig. 8. Constant  $a$ , measured by the slope of the plot, of course depends on the concentrations of the other components in the system, but

FIG. 10.

Initial oxygen absorption rates at 40.0° at different benzaldehyde concentrations.



Rates of absorption in ml. of oxygen (at N.T.P.)/min./mole of benzaldehyde.

Chlorobenzene used as diluent. Concentrations in g./10 ml. of solution.

Curve A :  $[\text{Bz}_2\text{O}_2] = 0.3000$ ;  $[p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OH}] = 0.000424$ ;  $[\text{Ph}\cdot\text{CO}_2\text{H}] = 1.78$ .

Curve B :  $[\text{Bz}_2\text{O}_2] = 0.3000$ ;  $[p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OH}] = 0.000636$ ;  $[\text{Ph}\cdot\text{CO}_2\text{H}] = 1.50$ .

$b$  and  $c$  should, from the modified form of equation (A), be independent constants indicative of the additional reactions postulated in (i) and (ii) above.

Fig. 9 shows that

$$1/\{-d[\text{O}_2]/dt\} \propto [\text{Ar}\cdot\text{OH}] + \text{constant}$$

where the constant, which clearly is indicative of the extent of chain termination not involving  $p$ -cresol, is so small that its nature can be ignored in our work.

Again, the experimental results plotted in Fig. 10 (obtained with benzaldehyde-chlorobenzene mixtures) show that the rate of oxidation is proportional to the second power of the benzaldehyde concentration, and Fig. 11 shows that it is dependent on the oxygen concentration in the following way :

$$[\text{O}_2]/\{-d[\text{O}_2]/dt\} = p[\text{O}_2] + q$$

*i.e.*,

$$-d[\text{O}_2]/dt = [\text{O}_2]/\{p[\text{O}_2] + q\}$$

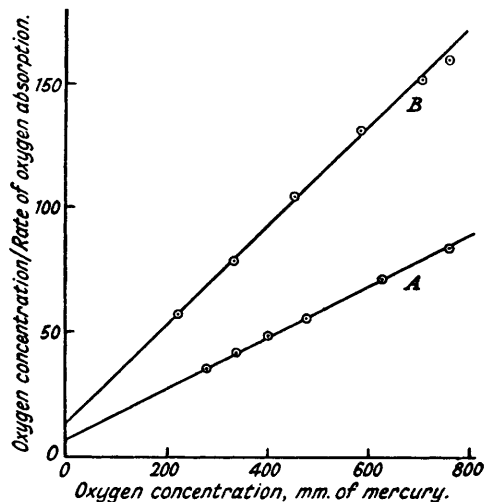
Ignoring that part of this relation which is independent of  $p$ -cresol (which, we have already shown, is very small), we find that, at atmospheric pressure,  $q$  is much smaller than  $p[\text{O}_2]$ ; for this reason, we have been unable to determine its kinetic dependence on other variables—any deviation from the experimental result,  $-d[\text{O}_2]/dt \propto [\text{RH}]^2$ , caused by this small term  $q$  would not show in Fig. 10.

Thus our experimental results substantiate our view that reactions (1)—(4) and (6)—(9) are the important ones occurring during the autoxidation of a benzaldehyde- $p$ -cresol system. There

is in addition, however, a very small denominator term which could perhaps be accounted for by the introduction of reaction (5). In this connection we would point out that we can expect the ratio  $k_3/k_4$  to be very large (cf. Bamford and Dewar, *Proc. Roy. Soc.*, 1949, **198**, A, 252), which would lead to the condition  $k_3k_6[O_2] \gg k_4k_5[RH]$ .

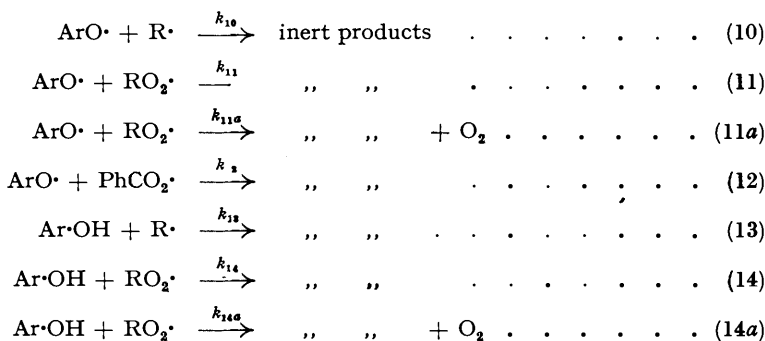
Although we have successfully compared our experimental results with the modified form of the kinetic equation (A) derived from the reactions (1)–(9), it is of interest to compare them also with alternative hypotheses. The natures of the radical-catalysed chain initiation and chain propagation processes are so well established by other workers on autoxidation that we need only

FIG. 11.  
Initial oxygen absorption rates at 40.0° at different oxygen concentrations.



Oxygen concentrations in mm. of Hg; rates of absorption in ml. (at N.T.P.)/min./mole of benzaldehyde. Concentrations in g./10 ml. of solution.  
Curve A :  $[Bz_2O_2] = 0.3000$ ;  $[p-C_6H_4Me \cdot OH] = 0.00212$ ;  $[Ph \cdot CO_2H] = 1.54$ . (10 ML. of Ph·CHO.)  
Curve B : Chlorobenzene used as diluent.  $[Bz_2O_2] = 0.3000$ ;  $[p-C_6H_4Me \cdot OH] = 0.00106$ ;  $[Ph \cdot CO_2H] = 1.50$ . (5 ML. of Ph·CHO + 5 ml. of PhCl.)

consider alternative chain termination reactions (which must, of course, involve *p*-cresol). Of these, the most plausible are given below :



In the Table, a summary of the kinetic equations derived by introducing each of these termination reactions, with and without chain transfer, is given. It is seen that our results cannot be explained by any likely reaction sequence other than that marked \*, which we have discussed in detail above.

It is interesting to note that reaction (12), which has in fact been found to occur by Cosgrove and Waters (*loc. cit.*, 1949), must be negligible in this autoxidation system. We suggest that this can be accounted for by the rapidity of reaction (2) involving the substrate, which in effect

prevents any appreciable number of  $\text{Ph}\cdot\text{CO}_2\cdot$  radicals from reacting with the few  $\text{ArO}\cdot$  radicals present in the mixture.

Reaction (14) has been postulated by Bolland and ten Have (*Trans. Faraday Soc.*, 1947, **43**, 201) for the inhibition of the autoxidation of ethyl linoleate by quinol. It is significant that it leads to different kinetics for the autoxidation process from those found by ourselves. This may well be due to the different degrees of reactivity of semi-quinol radicals ( $\text{Aryl-O}\cdot$ ) and semi-quinone radicals ( $\cdot\text{O-C}_6\text{H}_4\text{-O}\cdot$ ), and also to the difference in the ease of dehydrogenation of the two autoxidising liquids.

Chain-transfer reactions.	Chain-termination reactions.	Approximations (if any).	Proportionality of $-d[\text{O}_2]/dt$ to:			
			$[\text{RH}]$ .	$[\text{ArOH}]$ .	$[\text{O}_2]$ .	$[\text{Bz}_2\text{O}_2]$ .
* (5), (6), & (7)	(8) & (9)	$k_4[\text{RH}] \gg k_6[\text{Ar}\cdot\text{OH}]$ $k_7[\text{RH}] \gg k_8[\text{ArO}\cdot] + k_9$	$\frac{[\text{RH}]^2}{\alpha + \beta[\text{RH}]}$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$\frac{[\text{O}_2]}{\alpha[\text{O}_2] + \beta}$	$\frac{\{[\text{Bz}_2\text{O}_2] + \alpha\}}{-\beta}$
(5) & (7)	(10)	$k_7[\text{RH}] \gg k_{10}[\text{R}\cdot]$	$[\text{RH}]^{\frac{1}{2}}$	$[\text{Ar}\cdot\text{OH}]^{-\frac{1}{2}}$	$[\text{O}_2]$	$[\text{Bz}_2\text{O}_2]^{\frac{1}{2}}$
(5) & (7)	(11)	$k_7[\text{RH}] \gg k_{11}[\text{RO}_2\cdot]$	$[\text{RH}]$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]^{\frac{1}{2}}$	$[\text{Bz}_2\text{O}_2]^{\frac{1}{2}}$
(5) & (7)	(11a)	$k_7[\text{RH}] \gg k_{11a}[\text{RO}_2\cdot]$	$\alpha[\text{RH}] - \beta$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} - \beta$	$\alpha[\text{O}_2]^{\frac{1}{2}} - \beta$	$\alpha[\text{Bz}_2\text{O}_2]^{\frac{1}{2}} - \beta[\text{Bz}_2\text{O}_2]$
(6) & (7)	(10)	$k_4[\text{RH}] \gg k_6[\text{Ar}\cdot\text{OH}]$ $k_7[\text{RH}] \gg k_{10}[\text{R}\cdot]$	$[\text{RH}]$	$[\text{Ar}\cdot\text{OH}]^{-\frac{1}{2}}$	$[\text{O}_2]^{\frac{1}{2}}$	$[\text{Bz}_2\text{O}_2]^{\frac{1}{2}}$
(6) & (7)	(11)	$k_4[\text{RH}] \gg k_6[\text{Ar}\cdot\text{OH}]$ $k_7[\text{RH}] \gg k_{11}[\text{RO}_2\cdot]$	$[\text{RH}]^{3/2}$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]^{\frac{1}{2}}$
(6) & (7)	(11a)	$k_4[\text{RH}] \gg k_6[\text{Ar}\cdot\text{OH}]$ $k_7[\text{RH}] \gg k_{11a}[\text{RO}_2\cdot]$	$\alpha[\text{RH}]^{3/2} - \beta$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} - \beta$	$[\text{O}_2]^0$	$\alpha[\text{Bz}_2\text{O}_2]^{\frac{1}{2}} - \beta[\text{Bz}_2\text{O}_2]$
(5) & (7)	(12)	$k_7[\text{RH}] \gg k_{12}[\text{Ph}\cdot\text{CO}_2\cdot]$	$[\text{RH}]^2$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]$	$[\text{Bz}_2\text{O}_2]^0$
(6) & (7)	(12)	$k_4[\text{RH}] \gg k_6[\text{Ar}\cdot\text{OH}]$ $k_7[\text{RH}] \gg k_{12}[\text{Ph}\cdot\text{CO}_2\cdot]$	$[\text{RH}]^3$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]^0$
none	(5), (10), & (11)	none	$[\text{RH}]^0$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]$	$[\text{Bz}_2\text{O}_2]$
none	(5) & (11a)	none	$[\text{RH}]^0$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} - \beta$	$\alpha[\text{O}_2] - \beta$	$[\text{Bz}_2\text{O}_2]$
none	(6) & (10)	none	$\alpha[\text{RH}] + \beta$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} + \beta$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]$
none	(6) & (11)	none	$\alpha[\text{RH}] + \beta$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} + \beta$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]$
none	(6) & (11a)	none	$\alpha[\text{RH}] + \beta$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} + \beta$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]$
none	(13)	none	$[\text{RH}]^0$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]$	$[\text{Bz}_2\text{O}_2]$
none	(14)	none	$\alpha[\text{RH}] + \beta$	$\alpha[\text{Ar}\cdot\text{OH}]^{-1} + \beta$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]$
none	(14a)	none	$[\text{RH}]$	$[\text{Ar}\cdot\text{OH}]^{-1}$	$[\text{O}_2]^0$	$[\text{Bz}_2\text{O}_2]$

#### EXPERIMENTAL.

*Purification of Materials.*—Benzaldehyde (B.P.C.) was kept over anhydrous potassium carbonate before being fractionally distilled under a reduced pressure of nitrogen into a blackened flask possessing a side-arm inlet tube with tap, through which nitrogen was passed whenever a sample of the benzaldehyde was subsequently pipetted out for use. Cylinder nitrogen was purified for this purpose by a train consisting of (a) two bottles of Fieser's solution (40 g. of potassium hydroxide, 8 g. of sodium anthraquinone- $\beta$ -sulphonate, and 30 g. of sodium dithionite in 200 ml. of water; Fieser, *J. Amer. Chem. Soc.*, 1924, **46**, 2639), (b) a bottle of saturated lead acetate solution, (c) a bottle of concentrated sulphuric acid, (d) a tower of potassium hydroxide pellets, and (e) a mercury "blow-off." The benzaldehyde purified in this way was shown by analysis to contain less than 0.15% of benzoic acid and less than 0.015% of peroxide.

*p*-Cresol was distilled under reduced pressure, and subsequently stored in a vacuum-desiccator over concentrated sulphuric acid. A standard solution of the compound in benzaldehyde was prepared whenever necessary by transferring a small glass cup containing an accurately weighed sample of *p*-cresol to a 500-ml. blackened flask possessing a side-arm inlet tube with tap. Purified nitrogen was passed through this flask whilst a known volume of benzaldehyde was transferred from the storage vessel by means of a pipette. The resulting solution was kept under nitrogen throughout.

Benzoyl peroxide was recrystallised from hot chloroform, and stored in a vacuum-desiccator over concentrated sulphuric acid; it had m. p. 101—102° (Found: peroxide content >98%). Benzoic acid and trichloroacetic acid were recrystallised and stored in a vacuum-desiccator over concentrated sulphuric acid. Chlorobenzene and pyridine were dried and fractionated before use.

*Measurement of Oxygen Absorption.*—The apparatus consisted essentially of a reaction vessel (a Pyrex-glass bulb of approx. diameter 4 cm., fitted with a neck *ca.* 18 cm. long and 1.4 cm. in diameter) connected by means of B.14 joints and flexible rubber pressure tubing to a glass manometric system. The latter consisted of a butyl phthalate manometer, a graduated gas burette of 50-ml. capacity containing mercury and provided with a levelling tube, and gas leads for the admission of dry oxygen and for evacuation of the system when required. Each portion of the apparatus could be controlled by a tap. The reaction vessel was placed in a closely-fitting black cloth bag to prevent light from entering the reaction mixture, and was shaken horizontally by an electrical shaker at a rate of about 900 cycles/min. with an amplitude of *ca.* 0.4 cm.; under these conditions the rate of oxygen diffusion through the liquid was greater than the rate of oxygen absorption, since duplicate pieces of apparatus operating at different shaking speeds gave concordant oxygen-uptake rates. The reaction vessel was immersed in a water-thermostat controlled to  $\pm 0.05^\circ$ .

The reaction vessel and pipettes were very carefully cleaned before each run with methanolic sodium hydroxide, followed by concentrated nitric acid. They were then rinsed well with distilled water and ethyl alcohol, and dried in the steam-oven.

For each run the procedure was as follows: A known amount of benzoic acid was weighed into the reaction vessel (placed in position as described above). A small, carefully cleaned glass cup, containing an accurately weighed sample of benzoyl peroxide, was introduced, followed by known volumes of the stock benzaldehyde and *p*-cresol solutions, discharged from pipettes to give a total volume of 10 ml. The reaction vessel was then quickly closed, and the whole system evacuated at the water pump for 1 minute without shaking and  $\frac{1}{2}$  minute with shaking. Cylinder oxygen, after traversing a mercury lute, a wash-bottle containing concentrated sulphuric acid, and a tower of phosphoric oxide, was introduced into the system, after which the gas burette was read at atmospheric pressure and the shaking recommenced. Subsequent burette readings were made at room temperature and atmospheric pressure at suitable time intervals, and were computed as ml. of oxygen at N.T.P./mole of benzaldehyde. It was necessary to make a slight correction for the oxygen physically dissolved in the liquid at the commencement of each run.

In the absence of benzaldehyde, a chloroform solution of equimolecular amounts of *p*-cresol and benzoyl peroxide showed no tendency to absorb oxygen when heated at  $30^\circ$ .

*Determination of Peroxide Values.*—The results given in Fig. 2 were obtained by measuring both the oxygen absorption and the peroxide values of a single reaction mixture (30 ml.). The former were obtained by the method described in the preceding section, shaking being stopped at suitable time intervals to allow a 1-ml. sample to be extracted with a pipette; the reaction vessel and manometric system were re-evacuated and refilled with oxygen before shaking was recommenced, the stop-clock timing the reaction being stopped and started simultaneously with the shaking.

Peroxide values were determined iodometrically by the technique used by Robertson and Waters (J., 1948, 1578) for the determination of tetralin hydroperoxide, in which iodine liberation was completed at  $80^\circ$  under a carbon dioxide atmosphere.

*Determination of the Reaction Kinetics.*—The experimental data of two operators (Mrs. A. M. B. and C. W. J.), using similar but independent sets of apparatus, have been combined in Figs. 7 A, 8 A, 9 A, B, C, and E, and 10 A. No distinction between the two is apparent.

*Initial rate of reaction.* This was computed as the average rate of oxygen absorption over the first 10.5 minutes, from the oxygen uptake figures at 1, 10, and 11 minutes. This proved to be more satisfactory than the noting of the time required for the absorption of a pre-determined volume of oxygen, since it was found to eliminate irregularities associated with the commencement of the reaction.

*Change in benzaldehyde concentration.* The results for this were obtained by diluting the benzaldehyde with chlorobenzene. Chlorobenzene is admirable for this purpose, since it will be comparatively inert towards the reacting mixture, and its molar concentration per unit volume is approximately the same as that of benzaldehyde; hence the molar concentrations of the reactants will be unaltered in Fig. 10 where the total initial volume of benzaldehyde and chlorobenzene remains constant.

*Change in oxygen concentration.* This was effected by connecting the "free" open side of the butyl phthalate manometer to a closed volume (carefully tested for leaks), whose pressure could be reduced to any constant value, read on a mercury manometer. Oxygen absorption measurements were then made at this known reduced pressure in the usual manner.

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