Studies of Inhibitor Action in the Photochemical Autoxidation of Benzaldehyde

I. Results with Hydroquinone and their Bearing on the Question of Chain Initiation

HANS L. J. BÄCKSTRÖM and ÜLO RIINER*

Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

Chain initiation in the photochemical autoxidation of liquid benzaldehyde is due to abstraction of a hydrogen atom by a light-activated benzaldehyde molecule from a benzaldehyde molecule in the ground state, leading to the formation of a benzoyl radical (I) and a phenyl-hydroxymethyl radical (II). As shown by measurements of triplet-state quenching, the reacting excited benzaldehyde molecules are mainly, but possibly not exclusively, in the triplet state. The mean life of triplet benzaldehyde in pure benzaldehyde at 18°C is *ca.* 3×10^{-9} sec. A trend in the observed values of the quenching constant may indicate that the reaction is fast enough to compete with the process of intersystem crossing.

In the photochemical autoxidation of benzaldehyde containing sufficient hydroquinone, benzoquinone and an organic peroxide are formed in approximately equimolar quantities, as shown by iodometric titrations. The quantum yield of the induced oxidation of hydroquinone is found to be 0.5, showing that the absorption of a light quantum by benzaldehyde initiates only one reaction chain. This is suggested to be due to a reaction of radical II with benzaldehyde resulting, in the presence of oxygen, in the formation of an intramolecularly hydrogen-bonded peroxy radical which is incapable of hydrogen abstraction from either benzaldehyde or hydroquinone.

A n early paper by one of us on the chain mechanism in the autoxidation of aldehydes [1] included a short account of some preliminary measurements of the rate of the induced oxidation of a number of strong inhibitors under comparable conditions. (Ref. 1, p. 117.) Dilute solutions of the inhibitors in benzaldehyde were shaken with oxygen under constant irradiation, and the decrease in the inhibitor concentration with time was calculated from the

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* Present address: AB Karlshamns Oljefabriker, Karlshamn, Sweden.

resulting increase in the rate of oxygen absorption. The results showed that different inhibitors may be oxidized at widely different rates. From this it was concluded that the induced oxidation of the inhibitor does not in itself break the reaction chain but merely leads to an increased probability of chain breaking, by producing radicals not normally present in the reaction. Results on the dependence of reaction rates on light intensity pointed in the same direction.

Using the same kinetic method in combination with quantum efficiency determinations, as well as analytical and other methods, we have made a more detailed study of the induced oxidation of a few selected inhibitors that seemed of special interest. In the present paper we give the results obtained with hydroquinone, an inhibitor showing "ideal" behaviour. The results permit certain general conclusions to be drawn with regard to the mechanism of the photochemical autoxidation of benzaldehyde.

Two following papers in this series will deal with the induced oxidation of anthracene and 9-methyl-anthracene, respectively.

EXPERIMENTAL

Apparatus and procedure. Two different types of shaking apparatus were used. With apparatus No. 1, which has been described earlier,[2] a 4 ml sample of aldehyde in a quartz tube (length 10 cm, diameter 2.4 cm) was shaken vertically at a rate of 240 complete strokes per minute and with a stroke length of 8 cm. The tube was connected by means of vacuum tubing to a water-jacketed Hulett type gas burette that enabled the rate of oxygen absorption to be measured at atmospheric pressure. The shaking tube was immersed in a water bath furnished with a vertical quartz window. The temperature of the water bath was kept at $25.0 \pm 0.1°C$. The temperature of the gas burette was close to that of the laboratory ($21 \pm 1°C$) and was recorded at frequent intervals.

The light source was a vertical 220 V AC mercury arc, Luma LK 700, burned in series with a regulating resistance. Voltage variations were eliminated by means of a Sorensen voltage regulator. The light was passed through a filter combination with maximum transmission close to the mercury line at 313 mμ (1 cm of a solution of $NiSO_4$, 15 %, + $CoSO_4$, 12.5 %; 6 mm of Schott UG 11 filter glass; 1 cm 6.1×10^{-4} M K_2CrO_4 in 0.05 M KOH solution). To avoid undue heating of the nickel-cobalt sulfate solution, which was placed next to the lamp, it was made to circulate through the filter cell. The quantum composition of the transmitted light was estimated to be: 297 mμ, 4 %; 302 mμ, 22 %; 313 mμ, 72 %; 334 mμ, 2 %. For 99 % absorption of these wavelengths by benzaldehyde [3] a layer thickness of < 0.1 mm is sufficient. Light absorption by hydroquinone at the concentrations used in the kinetic experiments was negligible.[4]

The light intensity was varied by placing rectangular apertures of different height in front of the thermostat window, as well as by varying the distance between the lamp and the shaking tube. At least one actinometric determination by the ferrioxalate method was made in connexion with every run. For this purpose 10 ml of 0.012 M potassium ferrioxalate in 0.05 M sulfuric acid was shaken in air and irradiated for a known length of time.* The ferrous iron formed was determined as described by Hatchard and Parker.[5] The results were calculated on the basis of their recommended quantum yield of ferrous iron at 313 mμ, 1.24, and assuming complete light absorption.

Before a run the shaking tube was rinsed several times, first with 99.5 % ethanol and then with redistilled benzene. This was found to be the only procedure leading to reproducible results. Solutions of hydroquinone in benzaldehyde were prepared under

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* Identical results were obtained when the actinometer solution, after removal of dissolved oxygen, was shaken in pure nitrogen. These experiments were made in shaking apparatus No. 2 by C. Åquist.

nitrogen and 4 ml pipetted into the shaking tube, which was then filled with oxygen and attached to the oxygen-filled gas burette.

All work with aldehyde or actinometer solution was performed in light from dark-room lamps.

Apparatus No. 2 was essentially a copy of one described and illustrated in a paper by Bolland and Cooper.[6] It enabled the rate of oxygen absorption to be measured at different constant oxygen pressures. The solution to be irradiated was contained in a cylindrical quartz vessel fitted with optically flat windows (internal diameter 2.1 cm, optical depth 3 cm). The reaction vessel could be connected to the manostat system through a flexible glass spiral. During a run it was shaken horizontally along the light beam at a speed of 650 c/min with a maximum throw of ca. 2 cm. The volume of the cell was ca. 10.5 ml, that of the sample generally 10 ml.

The manostat system was immersed in a water thermostat with plane glass windows. It consisted of a differential di-butyl phthalate manometer, a gas burette made of tubing of accurately known bore (Veridia tubing from Chance Bros. Glass Works), and a small electrolytic cell with platinum electrodes, filled with saturated oxalic acid solution. During a run the differential manometer was used to indicate deviations from the chosen constant oxygen pressure in the apparatus. The upward movement of the mercury level in the gas burette was actuated by the evolution of gas from the electrolytic cell. The movement of the mercury level was followed by observation with a cathetometer. The levels of the differential manometer were observed through a fixed telescope with a micro-scale in the ocular.
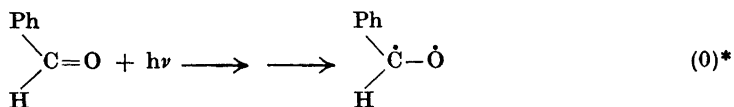
In the experiments reported in the present paper the temperature of the manostat system was $20.5 \pm 0.1°C$. The reaction vessel was maintained at $18.0 \pm 0.1°C$ by immersion in a thermostated tank fitted with a quartz window. It was irradiated with light of wavelength 366 mμ, isolated by means of 2 mm of Schott glass UG2 + 3 mm of window glass. The light source was a small AC mercury lamp, Luma LTU-120-S. The constancy of its radiation intensity at 366 mμ was checked by measurements with a thermopile and a galvanometer as described by Bäckström.[7]

Samples of solutions of hydroquinone in benzaldehyde were in this case transferred under nitrogen to the reaction vessel and were then degassed at 10^{-3} mm by the conventional freeze-pump-thaw technique, using solid CO_2 + ethanol as coolant. The evacuated cell was then connected to the manostat system, after which the whole system was evacuated and oxygen admitted to the desired pressure.
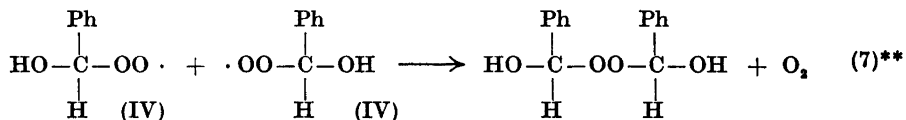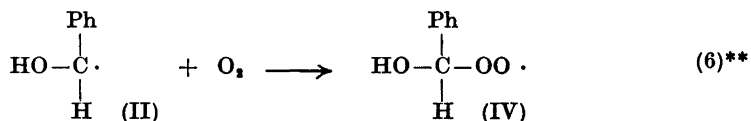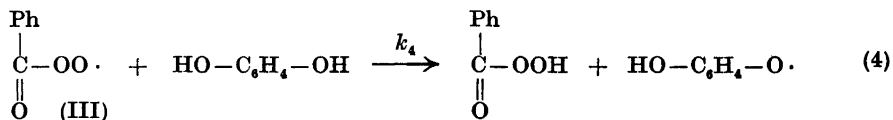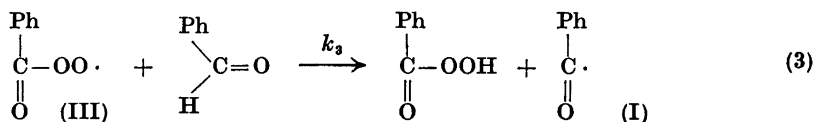
Materials. The chemicals used were of the highest purity commercially available. *Benzaldehyde* was further purified by fractional distillation under nitrogen at a pressure of 10 mm. It was stored in the dark under nitrogen for less than a week. *Hydroquinone* was recrystallized from ethanol. *Benzene* was fractionally distilled using a column corresponding to ca. 20 theoretical plates. *Naphthalene* was recrystallized three times from aqueous ethanol.

RESULTS AND DISCUSSION

It will be convenient to begin by presenting the reaction scheme which we find to be in general agreement with our results. The hydroquinone concentration is assumed to be sufficiently high for the normal chain termination mechanism, consisting in reactions between free radicals derived from the aldehyde, to be put out of play. A sufficiently high oxygen concentration is also postulated.

$$\begin{array}{c} Ph \\ \diagdown \\ \diagup \hspace{-0.3em} C=O \; + \; h\nu \; \longrightarrow \; \longrightarrow \\ H \end{array} \qquad \begin{array}{c} Ph \\ \diagdown \\ \diagup \hspace{-0.3em} \dot{C}-\dot{O} \\ H \end{array} \qquad\qquad (0)^*$$

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* See comments on page 634.

$$
\begin{array}{c}
\overset{Ph}{\underset{H}{>}}\dot{C}-\dot{O} \;+\; \overset{Ph}{\underset{H}{>}}C=O \;\xrightarrow{k_1}\; \overset{Ph}{\underset{O}{\overset{|}{C}}}\cdot \;+\; \cdot\overset{Ph}{\underset{H}{\overset{|}{C}}}-OH
\end{array}
\tag{1}
$$

(I)   (II)

$$
\overset{Ph}{\underset{O}{\overset{|}{C}}}\cdot \;+\; O_2 \;\xrightarrow{k_2}\; \overset{Ph}{\underset{O}{\overset{|}{C}}}-OO\cdot
\tag{2}
$$

(I)   (III)

$$
\overset{Ph}{\underset{O}{\overset{|}{C}}}-OO\cdot \;+\; \overset{Ph}{\underset{H}{>}}C=O \;\xrightarrow{k_3}\; \overset{Ph}{\underset{O}{\overset{|}{C}}}-OOH \;+\; \overset{Ph}{\underset{O}{\overset{|}{C}}}\cdot
\tag{3}
$$

(III)   (I)

$$
\overset{Ph}{\underset{O}{\overset{|}{C}}}-OO\cdot \;+\; HO-C_6H_4-OH \;\xrightarrow{k_4}\; \overset{Ph}{\underset{O}{\overset{|}{C}}}-OOH \;+\; HO-C_6H_4-O\cdot
\tag{4}
$$

(III)

$$
2\,HO-C_6H_4-O\cdot \;\longrightarrow\; HO-C_6H_4-OH \;+\; O=C_6H_4=O
\tag{5}
$$

$$
HO-\overset{Ph}{\underset{H}{\overset{|}{C}}}\cdot \;+\; O_2 \;\longrightarrow\; HO-\overset{Ph}{\underset{H}{\overset{|}{C}}}-OO\cdot
\tag{6**}
$$

(II)   (IV)

$$
HO-\overset{Ph}{\underset{H}{\overset{|}{C}}}-OO\cdot \;+\; \cdot OO-\overset{Ph}{\underset{H}{\overset{|}{C}}}-OH \;\longrightarrow\; HO-\overset{Ph}{\underset{H}{\overset{|}{C}}}-OO-\overset{Ph}{\underset{H}{\overset{|}{C}}}-OH \;+\; O_2
\tag{7**}
$$

(IV)   (IV)
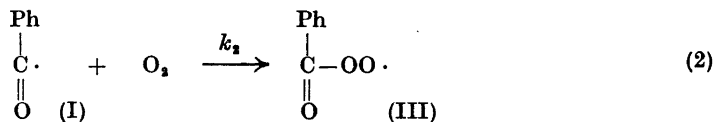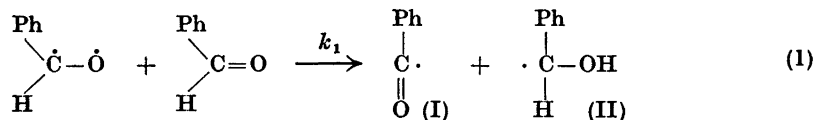
Assuming that the concentrations of the radicals reach stationary values, the following expression is obtained for the quantum efficiency of oxygen absorption:

$$
\varphi_{O_2} = 1.5 + \frac{k_3}{k_4}\frac{[\text{PhCHO}]}{c}
$$

where c stands for the concentration of hydroquinone. Also: $\varphi_Q = \varphi_P = 0.5$, where Q denotes quinone and P the peroxide formed in reaction (7).

As regards the chain initiating and propagating steps (0)—(3), the above reaction scheme does not differ from the one proposed earlier.[1] However, as the result of later studies of the spectra of carbonyl compounds, deeper insight has now been gained into the processes taking place when a molecule of one of these compounds absorbs a quantum of near ultraviolet light. Recent papers by Kasha [8] and Dörr [9] may be cited as key references. Of particular interest in the present connexion is a recent paper by Stockburger on the absorption
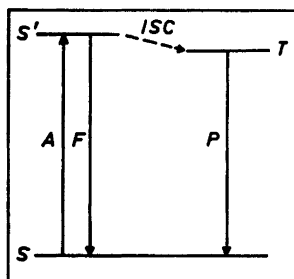


** Compare, however, p. 643 below.

Fig. 1. Schematic energy level diagram for the benzaldehyde molecule, showing transitions between the ground singlet level (S), the first excited singlet level (S') and the lowest triplet level (T). Solid arrows represent transitions involving radiation: A light absorption, F fluorescence, P phosphorescence. The dashed arrow represents radiationless intersystem crossing (I S C) from S' to T.

and emission spectra of benzaldehyde in the vapour state.[10] A schematic energy level diagram is shown in Fig. 1.

Absorption of a light quantum raises the molecule from its ground state S to the first excited singlet state S'. From this state it may either return to the ground state with emission of a light quantum (fluorescence), or may undergo a radiationless transition, termed intersystem crossing, to a triplet state T of somewhat lower energy. In this state the molecule has two electrons with parallel spins. The transition S' → T is therefore spin-forbidden but is made allowed by spin-orbit coupling and is, in fact, so rapid in aromatic carbonyl compounds that the S' → S transition is suppressed and no fluorescence is observed. From state T the molecule may return to the ground state with emission of a light quantum (phosphorescence). This transition is also spin-forbidden and a slow process. According to Stockburger the radiative lifetime of the T state of benzaldehyde has been found ≈ 2×10^{-3} sec. This long intrinsic lifetime will of course favour its participation in photochemical reactions, as will also the presence of the unpaired electrons.

Under suitable experimental conditions, i.e. in rigid solution at liquid air temperature, benzaldehyde like other aromatic carbonyl compounds therefore shows phosphorescence but no detectable fluorescence. If the latter statement is taken to imply that the ratio of the quantum yield of phosphorescence to that of fluorescence is ≥ 1000 (Kasha[11]), the lower limit of the rate of intersystem crossing may be estimated from a knowledge of the rate of the radiative transition S' → S. It has not been possible to measure this rate experimentally, but it may be estimated from the integrated intensity of the S → S' absorption. In this way Stockburger obtains a value of 1.6×10^{-6} sec for the radiative lifetime of the S'state, corresponding to a rate constant for the S' → S transition of 6×10^5 sec^{-1}. This gives a value of ≥ 6×10^8 sec^{-1} for the rate constant of the S' → T transition. The excited singlet state of benzaldehyde can therefore only be expected to take part in chemical reactions when the product of the rate constant and the concentration of the other reactant is at least of this order of magnitude. As will be shown in a later section, certain experimental results seem to indicate that the S' state may actually to some extent be involved in reaction (1). However, there can be no doubt that the excited benzaldehyde molecules taking part in reaction (1) are mainly, if not exclusively, in the triplet state. In step (0) its formula has been written as by Bäckström in 1934[1] and by Lewis and Kasha in 1944.[12] It will account

Fig. 2. The product $c_0(v_0)_{corr}$ *vs.* the intensity of the absorbed light (I) in einstein/min; c_0 = initial hydroquinone concentration in M, $(v_0)_{corr}$ = corrected initial rate of oxygen absorption in ml/min, obtained by extrapolation.
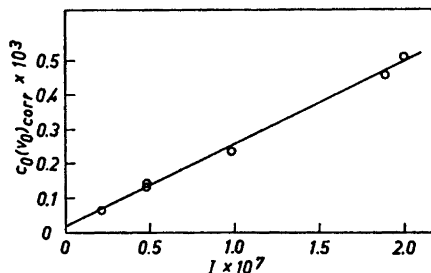
for its chemical reactions [1] and seems to be in agreement with spectral [9,13] and thermochemical [13] data. Compare, however, a recent paper by Kasha,[12] who finds the Lewis and Kasha structure inappropriate today.

In the following, experimental results will be presented and discussed in the order which appears most convenient.

The quantum yield of oxygen absorption. The first term in the expression for φ_{O_2} comes from the non-chain part of the reaction, represented by the above reaction scheme without step (3). If $(\varphi_{O_2} - 1.5)$ is denoted by φ_{corr}, the following relation should hold:

$$c \times \varphi_{corr} = \frac{k_3[\text{PhCHO}]}{k_4}$$

Fig. 2 gives the results of experiments where the initial hydroquinone concentration varied between 1.1×10^{-3} and 4.2×10^{-3} M. The product $c_0 \times (v_0)_{corr}$ is plotted *vs. I*, where $(v_0)_{corr}$ is the corrected initial rate of oxygen absorption expressed in ml/min, and I is the intensity of the absorbed light in einstein/min. The straight line corresponds to the equation:

$$c_0 \times (v_0)_{corr} = 0.014 \times 10^{-3} + 2.43 \times 10^3 \times I$$

The result indicates the presence of a slight dark reaction. For the quantum yield of the pure photochemical reaction the following expression is obtained:

$$\varphi_{O_2} = 1.5 + 0.101/c$$

Since for pure benzaldehyde [PhCHO] is 9.9 M, $k_3/k_4 = 1.02 \times 10^{-2}$.

Similar experiments were made with air instead of oxygen in the shaking tube, whereas the gas burette was filled with oxygen. They gave on the average 5 % lower rate values.

Determination of the rate of consumption of the inhibitor. As indicated in the introduction, the gradual increase in the rate of oxygen absorption as the result of the induced oxidation of a strong inhibitor may be used to measure the rate of the latter reaction. In the following it is assumed that the oxidation product has negligible inhibitor action; that the rate of chain initiation is constant; and that the inhibitor concentration c remains high enough, so that practically all the chains are broken as the result of the induced oxidation of the inhibitor. Under these conditions the following rate equations will hold:

$$v_{corr} = \frac{d(\text{O}_2)_{corr}}{dt} = \frac{A}{c} \qquad \text{(a)}$$

$$-\frac{dc}{dt} = B \qquad \qquad (b)$$

where v_{corr} is the rate of oxygen absorption in ml/min and $(O_2)_{corr}$ the total volume of oxygen absorbed in ml, both corrected for non-chain absorption. A and B are constants, characteristic of the inhibitor. Hence,

$$v_{corr} = A/(c_0 - Bt) \qquad \qquad (c)$$

where c_0 is the initial inhibitor concentration. Integration gives:

$$\log v_{corr} = \log (v_0)_{corr} + \frac{B}{A} \log e \, (O_2)_{corr}$$

Thus, if $\log v_{corr}$ is plotted against $(O_2)_{corr}$ a straight line is obtained. The intercept $= \log (v_0)_{corr}$ and the slope $S = (B/A) \log e$. Hence $B = 2.30 \, A \, S = 2.30 \, S \, c_0 \, (v_0)_{corr}$ mole $l^{-1}min^{-1}$.

The value of B may also be obtained in a different way. Eqn. (c) may be written

$$\frac{1}{v_{corr}} = \frac{1}{(v_0)_{corr}} - \frac{B}{A} t$$

A plot of $1/v_{corr}$ against t will therefore also give a straight line. The value of B is obtained from the relation:

$$B = -c_0 \frac{slope}{intercept}$$

This procedure is somewhat simpler. However, owing to unavoidable errors in reading the gas burette, it may in certain cases be easier to draw the best straight line on a diagram of the first kind.

The product $V \times B$, where V is the volume of the aldehyde in l, gives the number of moles of inhibitor oxidized per minute. Knowing the number of quanta absorbed in the same time, the quantum yield of the induced oxidation of the inhibitor may be calculated.*

A number of determinations of the quantum yield of the induced oxidation of hydroquinone were made by this method. The old shaking tube, which had given very low dark rates (see Fig. 2), had accidentally been broken, and the new shaking tubes gave high and irregular, although gradually decreasing dark rates. The best way out of this difficulty seemed to be to utilize the previous results for the pure photochemical reaction in order to calculate the total rate of chain initiation, R_i, from the rate of oxygen absorption. The values of R_i obtained in this way are equivalent to calculated light intensities and have been used in calculating the quantum yield of the induced oxidation of the inhibitor, φ_{H_2Q}.

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* If the mode of action of a suitable inhibitor may be regarded as known, and consequently the number of chains broken as the result of the induced oxidation of one inhibitor molecule, the method described may instead be used, in studying the kinetics of an autoxidation reaction, to determine the rate of chain initiation. This has been done successfully by George, Rideal and Robertson,[15] Bolland and ten Have,[16] Cooper and Melville,[17] and others. In several cases hydroquinone was used as inhibitor and the plausible assumption was made that one molecule breaks two chains.
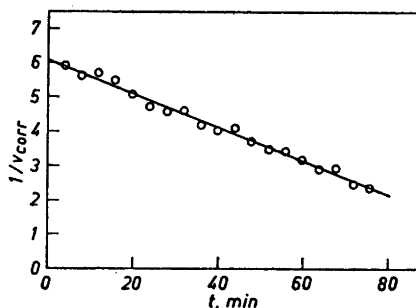
Fig. 3. $1/v_{corr}$ *vs.* time in min; v_{corr} = corrected rate of oxygen absorption in ml/min.
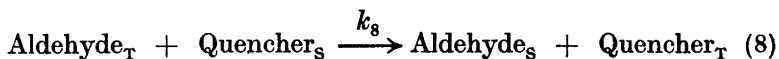
The method of calculation will be illustrated by an example. A plot of $1/v$ against t gave as a preliminary value: v_0 = 0.166 ml/min. The value of c_0 was 1.65×10^{-3} M. Applying the relation: $v_0 = 24.1 \times 10^3 [1.5 + (0.101/c_0)] R_i$, where 24.1×10^3 is the molar volume, expressed in ml, of oxygen at 21°C and atmospheric pressure, a preliminary value of R_i, 1.10×10^{-7} einstein per minute (E/min) is obtained. With this value of R_i the correction for non-chain absorption becomes 4.0×10^{-3} ml/min. A plot of $1/v_{corr}$ against t is shown in Fig. 3. The straight line drawn has the intercept 6.09 min/ml and the slope -4.91×10^{-2} ml^{-1}. The former value gives 1.11×10^{-7} E/min as the final value of R_i. Slope and intercept combined give $B = 1.33 \times 10^{-5}$ M min^{-1}. Finally, since the volume of the sample was 4 ml, $\varphi_{H_2Q} = 4 \times 10^{-3} \times B/R_i = 0.48$.

The results of twelve runs with two different shaking tubes are listed in chronological order in Table 1. They show beyond doubt that the quantum yield of the induced oxidation is 0.5, a result which was to be expected, provided the absorption of a light quantum starts one reaction chain. We shall return to this point later. A tendency towards increasing values of φ with increasing percentage of dark reaction may indicate that the presence of catalysts not only increased the number of chains started but also led to some direct oxidation of hydroquinone.

Quenching by transfer of triplet state energy. The reaction scheme presented does not take into account a process which may be of importance in certain cases, namely, the transfer of excitation energy from benzaldehyde molecules in the triplet state to other molecules present with comparable or lower triplet state energies. It may be represented schematically by the equation

Table 1. Quantum yield of the induced oxidation of hydroquinone.

	Tube 1						Tube 2					
c_0, mM	1.89	1.89	1.75	1.75	1.65	1.65	2.00	1.99	1.99	1.75	1.65	1.73
I, E/min $\times 10^8$	9.0	8.9	9.0	9.0	8.8	9.5	10.0	10.3	10.0	9.5	9.4	10.0
R_i, " " "	16.2	12.7	11.2	12.4	10.7	11.1	13.8	14.6	13.6	12.5	10.8	11.8
Dark rate, %	44	30	20	27	18	14	28	29	26	24	13	15
φ_{H_2Q}	0.55	0.53	0.50	0.48	0.45	0.48	0.49	0.55	0.54	0.49	0.45	0.44

$$\text{Aldehyde}_T \ + \ \text{Quencher}_S \ \xrightarrow{k_8} \ \text{Aldehyde}_S \ + \ \text{Quencher}_T \quad (8)$$

where the subscripts T and S indicate the spectroscopic state of the molecule, triplet or lowest singlet. This process will compete with reaction (1) and will lead to a reduction of the number of chains started in the ratio

$$1/(1 \ + \ \frac{k_8[\text{Quencher}]}{k_1[\text{Aldehyde}]}).$$

The magnitude of the rate constant k_8 depends mainly on the value of the triplet state energy (E_T) of the quencher. As shown by Bäckström and Sandros,[18] the rate of transfer of triplet state energy may in favourable cases be so high that the observed rate constant is close to the limit which in solution is set by the rate of diffusion. The rate constant of a diffusion-controlled bimolecular process in solution may be estimated by Debye's formula,[19] $k_d = 8RT/3000 \ \eta$ l mole^{-1} sec^{-1}, where η is the viscosity in poise and $R = 8.31 \times 10^7$ erg/°K. According to this formula, which has proved to be a remarkably successful approximation,* the rate constant is the same for different pairs of molecules. The maximum effect on the quantum yield due to quenching of this type may therefore be estimated if the value of $k_d/k_1[\text{Ald}]$ is known from experiments with a suitable quencher, such as naphthalene. Its triplet state energy is so low that its quenching constant may, in the present case, confidently be assumed to be close to k_d. Further it is chemically highly inert, and it transmits ultraviolet light down to *ca.* 327 mμ and may therefore be used in experiments where the mercury line at 366 mμ is used as exciting light. Transfer of triplet state energy from benzaldehyde to naphthalene has been demonstrated by Terenin and Ermolaev as sensitized phosphorescence in solid solution at low temperature.[21]

The viscosity of benzaldehyde is given as 1.40×10^{-2} poise at 25°C.[22] From data for similar liquids [23] its value at 18°C may be expected to be about 8 % higher. The formula of Debye therefore gives: $k_d = 4.3 \times 10^9$ M^{-1} sec^{-1} at 18°C.

A list of triplet state energy values that are of interest in connexion with the present paper or with subsequent papers in this series is presented in Table 2.

The exact value of E_T for hydroquinone does not seem to be known. Its phosphorescence spectrum in solid solution at low temperature, shown in a paper by Zudin for wavelengths > 400 mμ,[24] consists of only one band with a peak at 427 mμ, corresponding to 23 400 cm^{-1}. It is evident from the diagram, however, that the band must have its origin below 400 mμ. Probably, therefore, E_T for hydroquinone is slightly higher than for benzaldehyde. This does not, however, exclude the possibility that it may be an efficient quencher at room temperature, provided that its triplet state lifetime in the solution is very short compared to that of benzaldehyde.[20,27]

For the rest of the quenchers listed in the table, the E_T-values are so much lower than for benzaldehyde that their quenching constants must be close to k_d.

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* For examples, see Ref. 12 and Sandros and Bäckström.[20]

Table 2. Triplet state energies, E_T.

	E_T, cm^{-1}	Ref.
Benzaldehyde	25 179	10
Hydroquinone	*ca.* 24 500?	24
p-Benzoquinone	18 530	25
Naphthalene	21 300	21
Anthracene	14 870	26
9-Metylanthracene	14 460	26

In the naphthalene experiments, rates of oxygen absorption were determined in apparatus No. 2 for pairs of solutions that were of identical composition, except that one of them contained naphthalene. The solutions were prepared under nitrogen. The samples shaken had a volume of 10 ml. For experimental reasons, a lower temperature had to be used than in the rest of the experiments, 18.0 ± 0.1°C. The oxygen pressure was 598−603 mm. Absolute light intensities were not determined, but the intensity was constant within ± 1 % throughout the series, as shown by galvanometer deflexions. The light was 96 % 366 mµ, 4 % 334 mµ. The results are presented in Table 3, where c_1 and c_2 are the concentrations of hydroquinone and naphthalene, respectively. The rates of oxygen absorption in the absence of naphthalene and in its presence are denoted by v_a and v_p, both expressed in mm/min on the cathetometer scale.

In calculating the results, we shall begin by assuming that the quenching constant of hydroquinone has the same value as for naphthalene. For several reasons the probable quenching effect of oxygen will be disregarded. Its concentration was low and constant throughout the series, 3.6×10^{-3} M.* In two similar cases, benzophenone [28] and biacetyl,[18] its quenching constant has been found to be only about 50 % of the diffusion-controlled value. Furthermore, the interaction between oxygen and triplet benzaldehyde may possibly lead to chemical reaction, and not simply to deactivation.[28]

The following equations should apply to v_a and v_p.

$$v_a = K \times \varphi_{O_2} \quad \frac{k_1[\text{Ald}]}{k_1[\text{Ald}] + k_d c_1} = K \times \varphi_{O_2} \frac{1}{1 + \alpha c_1} \qquad (e)$$

$$v_p = K \times \varphi_{O_2} \frac{1}{1 + \alpha(c_1 + c_2)} \qquad (f)$$

Table 3. Quenching effect of naphthalene.

Experiment No.	c_1 M × 10³	c_2 M × 10³	v_a mm/min	v_p mm/min	$\dfrac{v_p}{v_a}$	$\dfrac{k_d}{k_1[\text{Ald}]}$ M^{-1}
1a, 1p	4.63	49.7	1.10	0.68	0.618	13.2
2a, 2p	4.65	85.5	1.10	0.55	0.50	12.4
3a, 3p	5.00	150.5	1.02	0.39	0.382	11.4
4a, 4p	18.9	48.6	0.245	0.165	0.673	12.3

* Riiner, unpublished.

where $\alpha = k_d/k_1[\text{Ald}]$. The value of the constant K is the same throughout the series; φ_{O_2} is a function of the hydroquinone concentration but is a constant within each pair of runs. These equations lead to the following expression for α.

$$\alpha = \frac{1 - v_p/v_a}{c_2 v_p/v_a - c_1(1 - v_p/v_a)} \qquad (g)$$

The calculated values of α for naphthalene are given in the last column of Table 3. From the mean value, 12.3 M^{-1}, and $k_d = 4.3 \times 10^9\ \text{M}^{-1}$, the product $k_1[\text{Ald}]$ is found to be 3.5 $\times$ $10^8\ \text{sec}^{-1}$. The mean life of triplet benzaldehyde molecules in pure benzaldehyde therefore amounts to only 3 $\times$ 10^{-9} sec at 18°C.

As regards the quenching action of hydroquinone, it will be noted that its concentration was much higher in experiment 4 than in the others. The value of α calculated from this experiment, assuming that the quenching constant of hydroquinone has the same value as for naphthalene, coincides with the mean value from experiments 1—3. This is no longer the case if the calculation is based on the assumption that hydroquinone does not act as a quencher; the first three values in the table are lowered by 5—6 %, but the last by as much as 19 %. This indicates that hydroquinone is, in fact, a quencher besides being an inhibitor. More direct evidence on this point was obtained from determinations of the initial rate of oxygen absorption made in apparatus No. 1 at 25°C, and with [H₂Q] ranging from 11 to 28 mM. The observed rates were consistently lower than those calculated on the assumption that hydroquinone acted only as an inhibitor. The deviation increased with increasing [H₂Q] and amounted to 21 % at the highest concentration. The light intensity (0.71—0.96 μE/min) was considerably higher than in the experiments listed in Table 1. The reaction was estimated to be about 97 % photochemical. Taking the dark reaction into account, the results were in satisfactory agreement with a value $k_s/k_1[\text{Ald}] = ca.$ 10 M^{-1} for hydroquinone at 25°C.

Certain calculations presented above were based on the mean value of α obtained from Table 3. However, the values from experiments 1—3 show a pronounced trend which should be outside experimental error. This trend may be completely eliminated if it is assumed that about 10 % of the excited aldehyde molecules undergo reaction while still in the singlet state. The S′ level of benzaldehyde is considerably below that of naphthalene. Deactivation of benzaldehyde molecules in this state by transfer of the excitation energy to naphthalene molecules is therefore not to be expected. Probably the same applies to hydroquinone. On this basis the previous eqns. (e) and (f) are replaced by the following, where β denotes the fraction of the excited aldehyde molecules reacting in the singlet state.

$$v_a = K \times \varphi_{O_2} \left[\beta + \frac{1 - \beta}{1 + \alpha\, c_1} \right]$$

$$v_p = K \times \varphi_{O_2} \left[\beta + \frac{1 - \beta}{1 + \alpha(c_1 + c_2)} \right]$$

From these equations it follows that if $K\ \varphi_{O_2}\ \beta$ is subtracted from v_a and v_p, the resulting "corrected" values, v_a' and v_p', may be substituted into eqn. (g) to find the value of α. The corrections have to be proportional to φ_{O_2}, and a difficulty in the present case is that the values of φ_{O_2} at 18°C, corresponding to different hydroquinone concentrations, are not known. However, in experiments 1—3 the values of c_1 were low, corresponding to chain lengths at 25°C of about 20. In trying out different sets of "corrections", they could therefore with sufficient accuracy be set equal to a fixed percentage of v_a. The trend was found to be most successfully eliminated when the "correction" applied was 10.5 % of v_a. The resulting values of α from experiments 1—3 were 16.1, 15.9, and 16.0 M^{-1}.

For the present, the explanation offered must be regarded as tentative. Further work is being planned to test its validity.

Reaction products. Analyses for reaction products were performed on relatively concentrated solutions of hydroquinone in benzaldehyde, that had been shaken with oxygen in apparatus No. 1 at 25°C for long periods, while irradiated with light of wavelength 313 mμ. Before being analyzed they were kept in the dark under nitrogen until all the peracid had disappeared by reaction with aldehyde. Evidence for the presence of quinone was obtained using a colour test described by Täufel and Gran.[29] Iodometric determinations showed that quinone and a peroxide had been formed in approximately equal quantities, as required by the reaction scheme.

Titrations were made in a nitrogen atmosphere on 1 ml samples, using an Agla micrometer syringe to deliver the titrating liquid.

In determining *benzoic acid* the sample was added to a mixture of 10 ml of ethanol + 3 ml of water, that had been flushed with nitrogen, and then titrated with 0.2 M NaOH, using bromothymol blue as indicator. — In determining the sum of *quinone* and *peroxide*, the sample was added to a mixture of 10 ml of ethanol, 3 ml of water, and 1 ml of hydrochloric acid (1:10), that had been similarly deaerated by flushing with nitrogen. After adding 2.5 ml of deaerated potassium iodide solution (1 g/ml) the liberated iodine was titrated with standard thiosulfate solution, the disappearance of the iodine colour being used to indicate the end point. Model experiments with quinone showed that about 15 min were required for the reaction to go to completion.

In one case quinone and peroxide were determined separately by the following procedure. A 2 ml sample of the solution was mixed with 5 ml of benzene and extracted repeatedly with 10 ml of water in a small separatory funnel. In the water layers the sum of quinone (Q)[30] and peroxide (P) was determined iodometrically, using starch as indicator. The results of the titrations are presented in column 2 of Table 4, where the volumes consumed are given in mm on the micrometer scale and per ml of the original solution, 1 mm corresponding to 0.02 ml of 0.191 M thiosulfate solution. The sum of Q and P in the original solution corresponded to 7.95 mm/ml, as determined by a separate titration. Using this value, the sum of Q and P remaining in the benzene layer after the extractions could be calculated. The results are given in column 3. Column 4 gives the ratio of $(Q + P)$ in the water phase to the corresponding value in the benzene phase. The decreasing values of this ratio are all higher than the corresponding value for quinone. A 2 ml sample of an unoxidized solution of hydroquinone in benzaldehyde, to which a small quantity of quinone had been added, was subjected to the same treatment. The results showed that the corresponding ratio was constant and equal to 0.125. The last value in column 4 indicates that only a small quantity of peroxide remained in the benzene layer after the fifth extraction. Estimating this quantity to correspond to 0.08 mm/ml, the concentration of quinone in the oxidized hydroquinone solution is found

Table 4. Separation of quinone (Q) and peroxide (P) by repeated extractions with water.

Extraction No.	$P + Q$, mm Water layer	$P + Q$, mm Benzene layer	Ratio	Calculated values Q_B	P_B	Q_W	P_W	P_W/P_B
1	2.91	5.04	0.58	3.33	1.71	0.42	2.49	1.46
2	1.25	3.79	0.33	2.96	0.83	0.37	0.88	1.06
3	0.76	3.03	0.25	2.63	0.40	0.33	0.43	1.08
4	0.52	2.51	0.21	2.34	0.17	0.29	0.23	1.35
5	0.35	2.16	0.16	2.08	0.08	0.26	0.09	1.1

Table 5. Results of analytical experiments.

c_0 μM/ml	Radiation dose, D μE/ml	Benzoic acid formed, $[B]$ μM/ml	$[Q + P]$ μM/ml	Oxygen absorbed μM/ml	$\dfrac{[B]_{obs}}{[B]_{calc}}$	$\dfrac{[Q + P]}{D}$	Oxygen accounted for, %
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
20.6	20.5	184	14.4	105.5	0.65	0.70	94.0
19.6	15.7	152.9	10.2	86.1	0.70	0.65	94.8
19.8	18.3	193.8	13.6	107.8	0.74	0.74	96.2
20.8	20.8	202.0	15.2	112.2	0.70	0.73	96.8
35.8	29.3	167.4	21.2	98.8	0.66	0.72	95.4

to correspond to $2.08 \times 1.125^5 = 3.75$ mm/ml, and consequently that of peroxide to 4.20 mm/ml. The figures presented in columns 5—9 have been calculated on the basis of the former of these values and from those in columns 2 and 3. The subscripts B and W refer to the benzene layer and the water layer, respectively.

It is evident from columns 6 and 9 of Table 4 that the peroxide present cannot be H_2O_2, which would have been extracted considerably more efficiently. (*Cf.* Bäckström and Beatty.[31])

The hydroquinone solution used in the above experiment was 21.2 mM and had received a radiation dose of about 20 μE/ml. Table 5 gives the results of similar experiments where the concentrations of quinone and peroxide were not determined separately but only their sum, $[Q + P]$.

The reaction scheme, together with previous experimental results, gives the following relations between the absorbed radiation dose (D) and the quantities of reaction products to be expected.
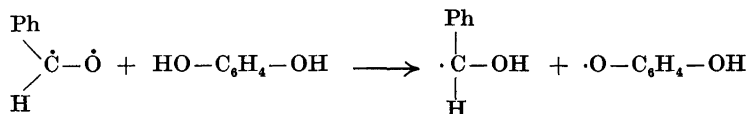
$$[B]_{calc.} = 2(1 + 0.101/c) \times D; \ [Q + P]_{calc.} = D$$

where B stands for benzoic acid and c is the average concentration of hydroquinone during the run. Putting $c = c_0 - \frac{1}{4}[Q + P]$ gives the ratios between observed and calculated quantities of benzoic acid listed in column 6. The average is 0.69. The average of the corresponding ratios for the sum of quinone and peroxide (column 7) is 0.71. These reaction products are therefore formed very nearly in the ratio required by the reaction scheme; but it is evident that only about 70 % of the light absorbed was effective in starting reaction chains. A deficit in the quantum yield of approximately 0.15—0.24 may be explained as the result of triplet state quenching (*cf.* page 640), and light absorption by hydroquinone may account for 0.02—0.04. A possible contributing factor is the formation of light-absorbing secondary reaction products. As shown by column 8, the analytically determined reaction products will account for only about 95 % of the oxygen absorbed.

Solutions of quinone in organic solvents (ethanol, benzene, petroleum ether) show an absorption band with maximum absorption in the region 430—460 mμ. The molar extinction coefficient ε is low, however, amounting to 17—20 at the maximum and 10—12 at 400 mμ.[32] Absorption curves of oxidized solutions of hydroquinone in benzaldehyde, measured against pure benzaldehyde, showed that the light absorption at 400 mμ corresponded to values of ε exceeding 200, calculated per mole of hydroquinone oxidized.

Throughout the wavelength region in question the light absorption was strong enough to obscure any structure due to quinone present. The spectrum did not resemble that of quinhydrone, nor is measurable absorption due to formation of quinhydrone to be expected at the concentrations used in this work.[32] Model experiments on solutions of quinone in benzaldehyde, with or without the presence of hydroquinone, led to the conclusion that the spectrum observed was probably due to the presence of small quantities of strongly absorbing secondary reaction products, formed from quinone under the influence of light and oxygen. Similar observations have been made by Schjånberg on solutions of quinone in water or ethanol.[4]
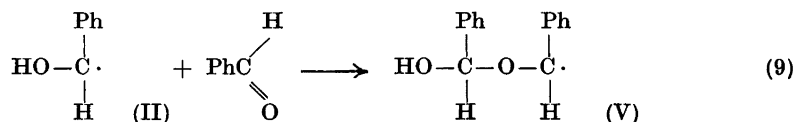
A possibility [18,20] which we have not discussed previously, and which seems to be ruled out by the analytical results, is that the quenching action of hydroquinone might be due to a chemical reaction with triplet benzaldehyde:

$$\begin{array}{c} \text{Ph} \\ \diagdown \\ \quad \dot{\text{C}}-\dot{\text{O}} \;+\; \text{HO}-\text{C}_6\text{H}_4-\text{OH} \;\longrightarrow\; \cdot\dot{\text{C}}-\text{OH} \;+\; \cdot\text{O}-\text{C}_6\text{H}_4-\text{OH} \\ \diagup \\ \text{H} \end{array}$$
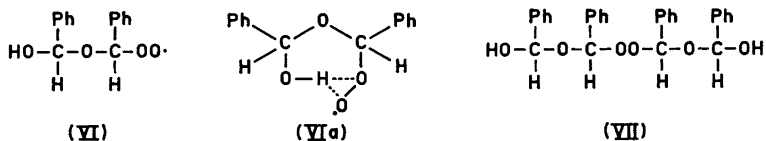
This reaction would be followed by reactions (5), (6), and (7) of the reaction scheme, and would therefore lead to the formation of quinone and peroxide, without any formation of benzoic acid.

The quantum yield of chain initiation. The fact that the quantum yield of the induced oxidation of hydroquinone is 0.5, inevitably leads to the conclusion that a light quantum absorbed by the aldehyde initiates only one reaction chain. This is by no means self-evident. The two radicals formed in the primary reaction (1) should both be capable of adding an oxygen molecule. The above-mentioned result implies that one of the peroxy radicals thus formed (IV) is incapable of abstracting a hydrogen atom from either benzaldehyde or hydroquinone. The following considerations seem to offer a possible explanation for this abnormal lack of reactivity.

There is reason to believe that radical II may react with benzaldehyde according to

$$\begin{array}{c} \text{Ph} \qquad\qquad \text{H} \qquad\qquad \text{Ph}\quad\ \text{Ph} \\ | \qquad\qquad\quad / \qquad\qquad\quad | \qquad\quad\ | \\ \text{HO}-\text{C}\cdot \;\;+\; \text{PhC} \;\;\longrightarrow\;\; \text{HO}-\text{C}-\text{O}-\text{C}\cdot \\ | \qquad\qquad\quad \diagdown\diagdown \qquad\qquad | \qquad\quad\ | \\ \text{H}\ \ (\text{II}) \qquad \text{O} \qquad\qquad\quad \text{H}\qquad\ \text{H}\ \ (\text{V}) \end{array} \qquad (9)$$

Reactions of this type, where a free radical with a lone electron on carbon adds to the oxygen of the carbonyl group of an aldehyde or a ketone, are known from the literature.[33,34] In pure benzaldehyde, reaction (9) may be assumed to be fast compared to the reaction of (II) with oxygen. Subsequent addition of oxygen to radical V would give the peroxy radical VI.

$$\begin{array}{ccc}
\begin{array}{c} \text{Ph}\ \ \text{Ph} \\ |\quad\ \ | \\ \text{HO}-\text{C}-\text{O}-\text{C}-\text{OO}\cdot \\ |\quad\ \ | \\ \text{H}\quad\ \text{H} \end{array}
&
\begin{array}{c} \text{Ph}\diagdown\ \ \ \text{O}\ \ \diagup\text{Ph} \\ \quad\text{C}\qquad\text{C} \\ \text{H}\diagup\ \ \text{O}-\text{H}\text{---}\text{O}\ \diagdown\text{H} \\ \qquad\qquad | \\ \qquad\qquad \text{O} \end{array}
&
\begin{array}{c} \text{Ph}\ \ \text{Ph}\quad\ \text{Ph}\ \ \text{Ph} \\ |\quad\ \ |\qquad\quad |\quad\ \ | \\ \text{HO}-\text{C}-\text{O}-\text{C}-\text{OO}-\text{C}-\text{O}-\text{C}-\text{OH} \\ |\quad\ \ |\qquad\quad |\quad\ \ | \\ \text{H}\quad\ \text{H}\qquad\quad \text{H}\quad\ \text{H} \end{array}
\\
(\text{VI}) & (\text{VI}a) & (\text{VII})
\end{array}$$

In view of certain results obtained by Rust and Youngman,[35] it seems to be of great importance in the present connexion that in radical VI the hydroxyl group is not attached to the same carbon atom as the peroxy group. These

authors have presented evidence for substantial modification of peroxy radical properties by the proximity of a hydroxyl group, which they ascribe to intramolecular or intermolecular hydrogen bonding. In radical VI conditions are favourable for the formation of an intramolecular hydrogen bond (formula VI a). As shown by the results of Rust and Youngman, such a bond may be expected to cause a drastic reduction in reactivity as regards hydrogen atom abstraction from neighbouring molecules.

The formula of the peroxide, which is formed with a theoretical quantum yield of 0.5, would accordingly be that shown in formula (VII).

A reaction corresponding to (9) has been shown to take place between benzaldehyde and radical I at about 100°C.[36] We have found no indication that this reaction is fast enough under our conditions to compete with reaction (2).

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