

## The Photochemical Co-oxidation of Benzaldehyde with 2-Propanol and with Benzyl Alcohol

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The photochemical autoxidation of solutions of benzaldehyde in 2-propanol (IPA) and benzyl alcohol (BA) has been studied at 1°C using light absorbed only by the aldehyde. Quantum efficiencies of O<sub>2</sub> consumption and quantities of H<sub>2</sub>O<sub>2</sub> and peroxybenzoic acid formed were determined at different aldehyde concentrations and light intensities (*I*). In the main the results are in accord with a reaction scheme presented on p. 1434 (written so as to include the rapid addition of O<sub>2</sub> to the primarily formed radicals) to which we refer. Here *T* represents an excited benzaldehyde molecule in the <sup>3</sup>*n,π*\* state, and the alcohol is assumed to be PhCH<sub>2</sub>OH. In this case reaction (1) leads to the formation of two identical hydroxyperoxy radicals (I), whereas in the IPA case they are different. The results indicate, however, that these radicals are kinetically equivalent and that the same reaction scheme represents the results with both alcohols equally well.

At a given aldehyde concentration the ratio % peracid/% H<sub>2</sub>O<sub>2</sub> was independent of  $\phi(O_2)$ , showing that the ratio  $k_2/k_1$  must be  $=k_4/k_3$  within limits of error. In IPA this ratio was found to be =15, in BA=2.3. For  $k_6/k_5$  the corresponding values were 5 and 0.8, the latter value showing that under the experimental conditions the benzoylperoxy radical attacks PhCH<sub>2</sub>OH more readily than PhCHO.

The limiting values of  $\phi(H_2O_2)$  corresponding to  $1/\sqrt{I}=0$ , obtained by linear extrapolation, were independent of the aldehyde concentration, as required by the reaction scheme, but lower than the required value of 1, viz., ca. 0.80 in IPA and 0.32 in BA. Arguments are presented for the view that this may be caused by hydrogen bonding to alcohol polymers of aldehyde molecules in the <sup>3</sup>*n,π*\* state. — A further deviation from the reaction scheme is the anomalous increase in  $\phi(O_2)$  with increasing aldehyde concentration, which is more pronounced in IPA than in BA. This is tentatively suggested to be due to the formation of a hydrogen bonded complex between a radical I and a benzaldehyde molecule.

It has long been known that the autoxidation of aldehydes is retarded by alcohols. As mentioned in an earlier paper by one of us,<sup>1</sup> dealing with the chain mechanism in the autoxidation of aldehydes, some experiments on the photochemical autoxidation of liquid benzaldehyde in the presence of benzyl alcohol showed that the rate of oxygen consumption at high alcohol concentrations was approximately proportional to the square root of light intensity. This shows that the reaction taking place under these conditions must be a co-oxidation of aldehyde and alcohol, the length of the reaction chains being limited by second-order reactions between free radicals.

In the present paper we present the results of an investigation aiming at the elucidation of the mechanism of this photochemical co-oxidation. Two different alcohols, benzyl alcohol and 2-propanol, were studied. In order to obtain information concerning the nature of the chain-breaking reaction, the experiments had to be made under such conditions that the chains were short. They were therefore performed with more or less dilute solutions of benzaldehyde in the alcohol, the lower concentration limit being set by the requirement of complete absorption of the exciting light under the experimental conditions. In the case of 2-propanol the exciting light generally was the mercury line at 313 nm, which is transmitted by this alcohol and is more strongly absorbed by the aldehyde than the 366 nm line. This made it possible to make experiments at lower aldehyde concentrations than in benzyl alcohol.

Quantum efficiencies of oxygen consumption were determined at different light intensities and aldehyde concentrations. Quantities of oxidation products formed were determined by analysis.

## EXPERIMENTAL

*Apparatus and procedure.* Degassed solutions of benzaldehyde in the alcohol studied were shaken with oxygen at  $1.0 \pm 0.1^\circ\text{C}$  at constant pressure and constant light intensity. The apparatus and procedure were, with a few exceptions mentioned below, the same as those described in an earlier paper from this laboratory,<sup>1</sup> to which we refer. (In Ref. 2 the apparatus used here is called apparatus No. 2.) The quantity of oxygen consumed in a run varied between 50 and 200  $\mu\text{moles}$ . The light source was in a number of preliminary runs a 125 W AC mercury lamp (Luma LTU-120-S). This lamp was later replaced by a 250 W AC mercury lamp (Luma Hg 250) surrounded by a Pyrex glass cooling jacket. In most experiments carried out at 313 nm a 200 W Point-source DC mercury lamp (Osram HBO 200 W/2) was used. The latter was enclosed in a lamphouse described by Calvert and Pitts.<sup>3</sup> The 366 nm line was isolated by means of a 6 mm Red Purple Corex glass + 3 mm window glass. The filter used to isolate the 313 nm line consisted of a 2 mm Schott glass UG 11 + 30 mm  $5.15 \times 10^{-4}$  M  $\text{K}_2\text{CrO}_4$  in 0.05 M KOH solution.

At least one actinometer run by the ferrioxalate method<sup>3</sup> was made in connection with every oxidation run. In the actinometer runs 10 ml of the actinometer solution was shaken under exactly the same conditions as in the main runs. Potassium ferrioxalate concentrations were 0.012 M at 366 nm and 0.006 M at 313 nm. Intensities were calculated on the basis of  $\phi(\text{Fe}^{2+}) = 1.26$  at 366 nm and 1.24 at 313 nm. During runs of both kinds, the intensity of a beam of light from the lamp, filtered as in the oxidation run, was measured at short intervals with an RCA 935 vacuum photodiode coupled to a galvanometer. This made it possible to correct for the rather small variations in light intensity. — Blackened brass gauze screens calibrated in a series of actinometer runs, served to decrease the intensity to 34 or 13 % of its maximum value. To prevent stray light from entering the solution the cell was enclosed in a thin-walled blackened brass casing which allowed light to enter only through the front window.

The volume of the reaction cell was *ca.* 12.5 ml. In early experiments the volume of the irradiated solution was 10 ml, and it was shaken at a speed of 650 c/min. The oxygen pressure was generally *ca.* 450 mm, but experiments at pressures down to 100 mm showed that the rate of oxygen consumption was independent of the pressure within limits of error (*cf.* p. 1439). A series of experiments with solutions in 2-propanol at  $p_{O_2}=450$  mm showed, however, that increasing the shaking speed to 950 c/min (the highest speed that could be used with safety) resulted in higher reaction rates when the aldehyde concentration exceeded 1 M. In subsequent runs (at *ca.* 450 mm) this higher shaking speed was used throughout and, in order to increase the shaking efficiency further, the volume of the solution was often decreased to 8 ml or less. A lower limit was evidently set by the requirement that light absorption had to be complete. As illustrated in Figs. 3 and 4, a change (at constant intensity of incident light) of the volume used ( $V$ ) by a factor  $r$  influenced the quantum efficiency of oxygen consumption in the same way as a change of intensity of incident light by a factor  $1/r$  at constant  $V$ . This shows that the shaking satisfactorily fulfilled its dual purpose to maintain a sufficiently high oxygen concentration in the solution, and to equalize the concentrations of the peroxidic free radicals, whose reactions with each other break the reaction chains.

The solutions contained a known weight of benzaldehyde per unit volume. Alcohol concentrations were calculated from literature values of the densities of the three liquids at 20°C assuming that no change in volume occurred on mixing.

In a considerable number of cases the oxidized solution was subjected to iodometric analysis, using a micrometer syringe as buret. The solvent used in the analysis was 2-propanol-water (1:1). In this solvent peroxybenzoic acid is stable whereas hydroxyhydroperoxides are rapidly hydrolyzed to hydrogen peroxide and the corresponding aldehyde or ketone (*cf.* p. 1434). Peroxybenzoic acid reacts much more rapidly with iodide ion than  $H_2O_2$ , which makes it possible to determine these two substances separately. In an analysis a portion of the irradiated solution containing some 50  $\mu$ moles of peroxides was transferred to about 20 ml of 2-propanol-water solvent containing an accurately known quantity of benzoic acid, sufficient to furnish the necessary hydrogen ions. The solvent had previously been de-aerated by a current of nitrogen which was kept going during the whole analysis. To the mixture was added *ca.* 0.1 mmole of KI. Immediate titration of the liberated iodine with 0.25 N thiosulfate — the disappearance of the iodine colour indicating the end-point — gave a measure of the peroxybenzoic acid present. About 30 mmole of KI was then added and the iodine liberated was titrated after 45 min. Finally remaining benzoic acid was determined by titration with 0.25 N NaOH. Testing this procedure on mixtures containing known quantities of peroxybenzoic acid, benzoic acid, and hydrogen peroxide, these substances were recovered within  $\pm 0.5$   $\mu$ mole. From the analysis the quantities of  $H_2O_2$ , peroxybenzoic acid ( $P$ ), and benzoic acid ( $B$ ) present in the irradiated solution were calculated. On the assumption that all benzoic acid had been formed in a secondary reaction between peroxybenzoic acid and benzaldehyde, the quantity of peroxybenzoic acid formed primarily was  $P_0 = P + B/2$ .

In a series of early experiments with 2-propanol an attempt was made to determine the quantities of acetone present in the oxidized solutions. The procedure used was to destroy the peracid by the addition of KI and thiosulfate, after which the solution was diluted fivefold with pure methanol and subjected to fractional distillation in order to separate the acetone from the 2-propanol. A volume of distillate corresponding to about half the methanol added was collected and analyzed by the salicylaldehyde method, as described by Berntsson.<sup>4</sup> The results of model experiments were consistently somewhat low, occasionally by as much as 10%. Acetone determinations by this method on solutions from oxidation experiments indicated that acetone and  $H_2O_2$  were formed in equal quantities. For the ratio acetone/ $H_2O_2$  the analyses gave values between 0.9 and 1.1.

*Materials.* 2-Propanol, Baker's Analyzed, was fractionally distilled in a column corresponding to 15 theoretical plates. Benzaldehyde and benzyl alcohol, both Eastman White Label, were fractionally distilled under 10 mm of pure nitrogen in a simplified version of a column described by Debiais, Nielaue and Letort.<sup>5</sup> In our column the output was limited by a short vertical piece of thick-walled capillary tubing with one end placed directly under the condenser and the other end fused to a tube which went through the side of the column and led to the receivers. This device gave a constant reflux ratio at constant boiling rate. Boiling rates were chosen to give a reflux ratio of 10:1 or more. The column was 100 cm long and packed with glass helices. Peroxybenzoic acid was pre-

pared and purified as described by D'Ans, Mattner and Busse.\* The purified material contained 98 % peroxybenzoic acid and 2 % benzoic acid.

All solutions were handled in light from darkroom lamps. As vacuum grease was found to give long induction periods in the oxidation runs, efficient grease traps were included in the column and other kinds of apparatus wherever it was found necessary. Benzaldehyde was stored in the dark under vacuum at  $-78^{\circ}\text{C}$ . Benzyl alcohol was stored in the dark under nitrogen at  $-5^{\circ}\text{C}$ . Samples of benzaldehyde and benzyl alcohol were withdrawn under a current of nitrogen.

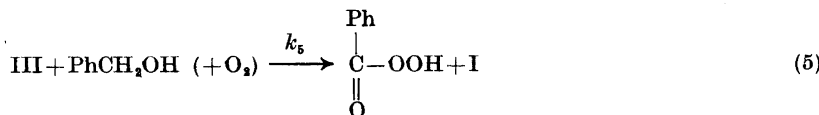
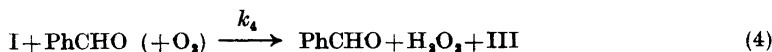
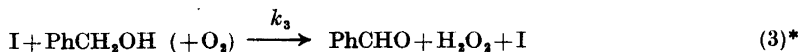
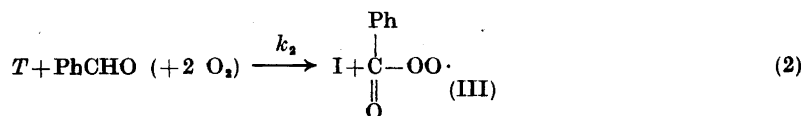
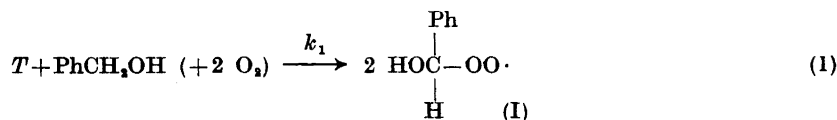
## RESULTS AND DISCUSSION

### Preliminary reaction scheme

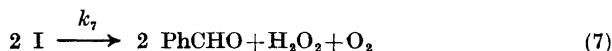
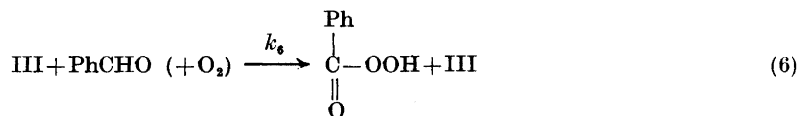
We shall begin by presenting a reaction scheme which will account for many of our results. The rate-determining steps are the formation of free radicals with a lone electron on carbon. Under the conditions of the experiments every such radical very rapidly adds an oxygen molecule to form the corresponding peroxide radical. For simplicity, the reaction steps are written in such a way as to include these secondary reactions. The number of oxygen molecules consumed is given in parenthesis.

The reaction scheme rests on the assumptions that absorption of a light quantum results in the excitation of the aldehyde molecule into a reactive triplet state which, for convenience, we shall denote by the letter *T*; and that deactivating processes are slow enough not to influence the results (*cf.* p. 1439).

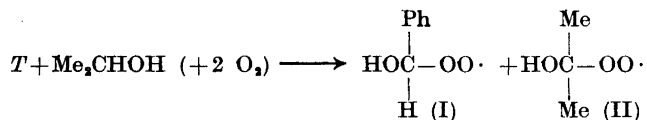
The reaction scheme for the case of *benzyl alcohol* is as follows.



\* The primary reaction product formed from radical I may be  $\alpha$ -hydroxybenzyl hydroperoxide which, however, may be expected to be decomposed by water and therefore to appear as  $\text{H}_2\text{O}_2$  in the iodometric analysis; *cf.* Schenk and Becker.<sup>7</sup>



The case of *2-propanol* is more complicated in that two different hydroxyperoxy radicals are formed as the result of the primary reaction corresponding to (1):



Furthermore, in reactions corresponding to (3), radicals I will be replaced by the alcohol-derived radical II. The resulting changes in the composition of the mixture of radicals will vary with the chain length and therefore with light intensity. However, there is reason to believe that these two radicals may be regarded as kinetically equivalent. On this assumption the same reaction scheme may be applied as in the case of benzyl alcohol. In fact, we find that it will account equally well for the results with the two alcohols.

According to the reaction scheme for *2-propanol*, acetone and  $\text{H}_2\text{O}_2$  will be formed in equal quantities. For simplicity, the term "radical I" will in the following be used also for the mixture of hydroxyperoxy radicals formed in this case.

At the lowest benzaldehyde concentrations where, as shown by Figs. 1 and 2, the aldehyde mainly acts as a sensitizer for the autoxidation of the alcohol, the chain-breaking reaction must evidently be a reaction between two radicals I, *i.e.*, reaction (7). Our results with regard to the quantum yield of  $\text{H}_2\text{O}_2$  formation at different light intensities indicate that reaction (7) must be the chain-breaking reaction within the whole concentration range investigated. A reaction between radicals I and III can not be expected to result in the formation of hydrogen peroxide.

Experimentally it was found that the quantum efficiency of oxygen consumption ( $\phi(\text{O}_2)$ ) at a given composition of the reaction mixture may be expressed as the sum of two terms,  $\phi(\text{O}_2) = a + b/\sqrt{I}$ , where  $I$  is the intensity of absorbed light in Einstein  $\text{l}^{-1}\text{min}^{-1}$ , and  $a$  and  $b$  are constants.

This is in agreement with the reaction scheme, which also shows that similar relations should hold for the quantum yields for the formation of hydrogen peroxide ( $\phi(\text{H}_2\text{O}_2)$ ) and of peroxybenzoic acid ( $\phi(\text{per})$ ). Thus, according to the reaction scheme:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = I + (k_3[\text{alc}] + k_4[\text{ald}])\sqrt{I/k_7}$$

where  $\sqrt{I/k_7}$  is the concentration of radical I. Therefore  $a(\text{H}_2\text{O}_2) = 1$ ,  $b(\text{H}_2\text{O}_2) = (k_3[\text{alc}] + k_4[\text{ald}])\sqrt{1/k_7}$ . Similarly for peracid:

$$a(\text{per}) = \frac{k_2[\text{ald}] \left(1 + \frac{k_6[\text{ald}]}{k_5[\text{alc}]}\right)}{k_1[\text{alc}] \left(1 + \frac{k_2[\text{ald}]}{k_1[\text{alc}]}\right)}$$

$$b(\text{per}) = k_4[\text{ald}] \left(1 + \frac{k_6[\text{ald}]}{k_5[\text{alc}]}\right) \sqrt{1/k_7}$$

Also  $a(\text{O}_2) = a(\text{H}_2\text{O}_2) + a(\text{per})$ ;  $b(\text{O}_2) = b(\text{H}_2\text{O}_2) + b(\text{per})$ .

A further experimental result is that the yields of  $\text{H}_2\text{O}_2$  and peracid, expressed in percent of oxygen consumed, are independent of the light intensity within limits of error. This applies down to the lowest observed values of  $\phi(\text{O}_2)$  (ca. 1.1–1.2 at the lowest aldehyde concentrations in the case of 2-propanol) where the value of  $\phi(\text{O}_2)$  is largely determined by the  $a$ -term, representing the chain-starting and chain-breaking reactions.

From the above expressions for the  $a$ - and  $b$ -values it follows that

$$\frac{a(\text{per})}{a(\text{H}_2\text{O}_2)} = \frac{k_2[\text{ald}] \left(1 + \frac{k_6[\text{ald}]}{k_5[\text{alc}]}\right)}{k_1[\text{alc}] \left(1 + \frac{k_2[\text{ald}]}{k_1[\text{alc}]}\right)}; \quad \frac{b(\text{per})}{b(\text{H}_2\text{O}_2)} = \frac{k_4[\text{ald}] \left(1 + \frac{k_6[\text{ald}]}{k_5[\text{alc}]}\right)}{k_3[\text{alc}] \left(1 + \frac{k_4[\text{ald}]}{k_3[\text{alc}]}\right)}$$

For the percentage yields to be independent of light intensity, it is necessary that the rate constant ratios  $k_2/k_1$  and  $k_4/k_3$  are equal. Our results show that this must be very nearly true. Under such conditions the same equation as for  $a(\text{per})/a(\text{H}_2\text{O}_2)$  and  $b(\text{per})/b(\text{H}_2\text{O}_2)$  should evidently be valid also for % peracid/%  $\text{H}_2\text{O}_2$ . Utilizing the mean values of these percentages at the different aldehyde concentrations used in the experiments with 2-propanol, and trying different values of  $k_2/k_1 = k_4/k_3$ , it was found that with an assumed value of 15 for this ratio a plot of

$\frac{\% \text{ peracid} \times [\text{alc}]}{\% \text{ H}_2\text{O}_2 \times [\text{ald}]} \times \left(1 + 15 \frac{[\text{ald}]}{[\text{alc}]}\right)$  vs.  $[\text{ald}]/[\text{alc}]$  gave a straight line with an

intercept of 15 and a slope corresponding to  $k_6/k_5 = 5$ . The agreement with the experimental values is shown by the full-drawn curves in the product distribution diagram from the experiments with 2-propanol, shown in Fig. 1. Similar calculated curves are shown in the corresponding diagram for benzyl alcohol (Fig. 2). They were calculated on the basis of  $k_2/k_1 = k_4/k_3 = 2.3$ ,  $k_6/k_5 = 0.8$ .

The results demonstrate the much greater ease with which hydrogen atoms are abstracted from benzyl alcohol than from 2-propanol. In part this may be due to the presence of two  $\alpha$ -hydrogen atoms in benzyl alcohol against only one in 2-propanol; but even calculated per  $\alpha$ -hydrogen atom, the rate of hydrogen abstraction by triplet benzaldehyde as well as by both peroxy radicals from benzyl alcohol is close to 3.2 times as high as from 2-propanol. As shown by the fact that in benzyl alcohol  $k_6/k_5$  is  $< 1$ , the benzoylperoxy radical actually reacts more readily with this alcohol than with benzaldehyde.

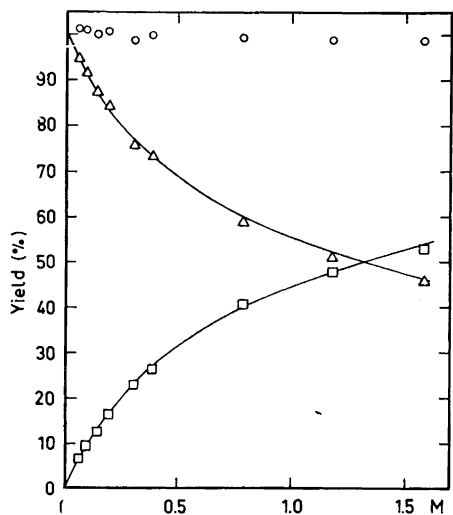


Fig. 1. Product distribution vs. aldehyde concentration in 2-propanol: Peroxybenzoic acid ( $\square$ ),  $\text{H}_2\text{O}_2$  ( $\Delta$ ), and peroxybenzoic acid +  $\text{H}_2\text{O}_2$  ( $\circ$ ), in % of oxygen consumed. All points represent means from several runs. Curves drawn are calculated.

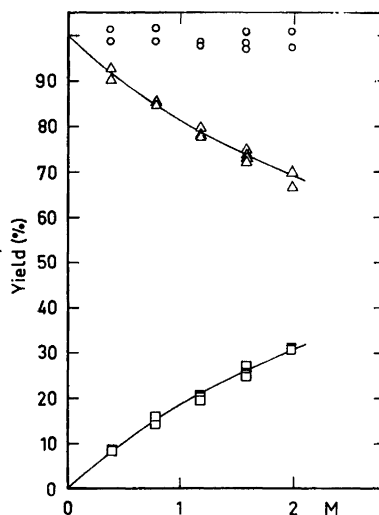


Fig. 2. Product distribution vs. aldehyde concentration in benzyl alcohol: Peroxybenzoic acid ( $\square$ ),  $\text{H}_2\text{O}_2$  ( $\Delta$ ), and peroxybenzoic acid +  $\text{H}_2\text{O}_2$  ( $\circ$ ), in % of oxygen consumed. Results from individual runs. Curves drawn are calculated.

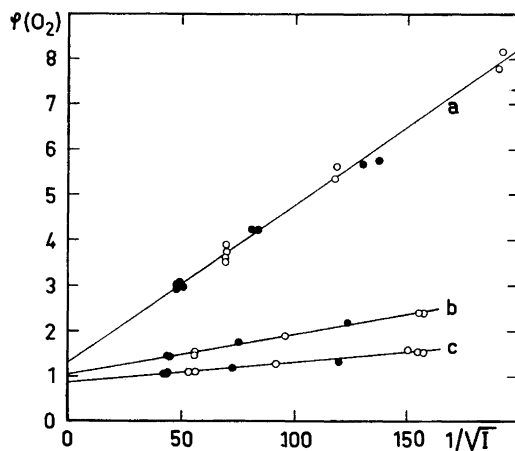


Fig. 3.  $\phi(\text{O}_2)$  vs.  $1/\sqrt{I}$  (with  $I$  in Einstein  $\text{l}^{-1} \text{min}^{-1}$ ) at different aldehyde concentrations in 2-propanol. Curve *a*, 1.18 M:  $\bullet$  volume of solution  $V=5$  ml;  $\circ$  10 ml. Curves *b*, 0.308 M, and *c*, 0.095 M:  $\bullet$   $V=5$  ml;  $\circ$  8 ml.

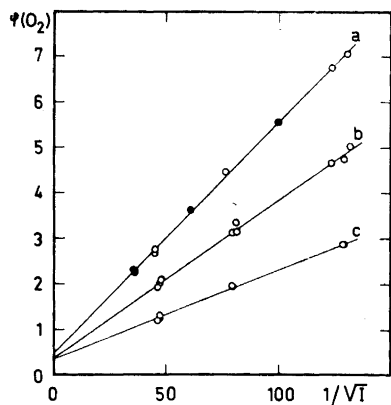


Fig. 4.  $\phi(\text{O}_2)$  vs.  $1/\sqrt{V}$  at different aldehyde concentrations in benzyl alcohol. Curve a, 1.99 M;  $\bullet$   $V=3$  ml;  $\circ$  5 ml. Curve b, 1.18 M,  $V=5$  ml. Curve c, 0.39 M,  $V=5$  ml.

Table 1.  $a$ - and  $b$ -values. 2-Propanol.

[PhCHO] (mole l <sup>-1</sup> )	Wave-length (nm)	$a$			$10^3 b$ (einstein <sup>1/2</sup> l <sup>-1/2</sup> min <sup>-1/2</sup> )		
		O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	peracid	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	peracid
1.58	366	1.70	0.77	0.90	50.2	23.0	26.6
1.18	366	1.31	0.67	0.63	34.5	17.6	16.5
0.785	366	1.19	0.70	0.48	22.3	13.1	9.1
0.390	313	1.12	0.82	0.30	10.3	7.5	2.7
0.308	313	1.05	0.80	0.24	8.7	6.6	2.0
0.196	313	0.97	0.81	0.16	6.0	5.1	0.9 <sub>0</sub>
0.144	313	0.92	0.81	0.12	5.6	4.9	0.7 <sub>1</sub>
0.095	313	0.87	0.80	0.08 <sub>1</sub>	4.5	4.1	0.4 <sub>1</sub>
0.063	313	0.85	0.81	0.05 <sub>7</sub>	3.8	3.6	0.2 <sub>0</sub>

Table 2.  $a$ - and  $b$ -values. Benzyl alcohol.

[PhCHO] (mole l <sup>-1</sup> )	Wave-length (nm)	$a$			$10^3 b$ (einstein <sup>1/2</sup> l <sup>-1/2</sup> min <sup>-1/2</sup> )		
		O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	peracid	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	peracid
1.99	366	0.45	0.31	0.14	51.1	34.9	15.9
1.58	366	0.46	0.34	0.12	43.2	31.9	11.1
1.18	366	0.38	0.30	0.07 <sub>7</sub>	34.7	27.3	7.0
0.781	366	0.38	0.32	0.05 <sub>0</sub>	26.1	22.2	4.0
0.390	366	0.34	0.32	0.03 <sub>0</sub>	19.7	18.0	1.7



The  $a$ - and  $b$ -values for oxygen consumption at a given aldehyde concentration were obtained by plotting the experimental  $\phi(\text{O}_2)$ -values *vs.*  $1/\sqrt{I}$  and calculating the best straight line by the method of least squares. Figs. 3 and 4 show such plots from experiments at three different aldehyde concentrations in 2-propanol and benzyl alcohol, respectively. Corresponding values of  $\phi$ ,  $a$  and  $b$  for peracid and  $\text{H}_2\text{O}_2$  were then obtained by multiplying with the average percentage yields of these reaction products at the concentrations in question. Tables 1 and 2 give the results for the two alcohols.

In an earlier study of the benzophenone-sensitized autoxidation of 2-propanol and certain other alcohols,<sup>8</sup> the rate of oxygen consumption was found to decrease with increasing oxygen pressure, due to deactivation of benzophenone molecules in the triplet excited state in collisions with oxygen molecules, occurring in competition with their reaction with the alcohol. No such effect was observed in benzyl alcohol, which was ascribed to the greater ease of hydrogen abstraction from this alcohol. In the present case a similar deactivation of triplet benzaldehyde should result in a lowering of the  $a$ -values by the factor

$$\left[ 1 + \frac{k_d \times p_{\text{O}_2}}{k_1[\text{alk}] + k_2[\text{ald}]} \right]^{-1}$$

where  $k_d$  denotes a deactivation constant, and of the corresponding  $b$ -values by the square root of the same factor. As mentioned in the experimental section, a number of comparative runs were made with both alcohols at oxygen pressures of 100 and 450 mm. The results showed no sign of an effect of this kind. The effect should evidently be particularly marked in 2-propanol at low benzaldehyde concentrations. However, in experiments at  $[\text{aldehyde}] = 0.20 \text{ M}$  and at different light intensities the same values of  $\phi_{\text{O}_2}$  were obtained at both pressures within limits of error.

#### Deviations from the reaction scheme

*The limiting quantum yield of  $\text{H}_2\text{O}_2$  formation.* As shown by the tables, the values found for  $a(\text{H}_2\text{O}_2)$  are, within limits of error, independent of the aldehyde concentration, which is in agreement with the reaction scheme. However, in both alcohols they deviate from the required value of 1.

Benzaldehyde as well as related ketones like acetophenone, when irradiated in solid solution at liquid air temperature, show phosphorescence but no detectable fluorescence. As pointed out by Kasha,<sup>9</sup> this shows that in molecules of these compounds the process of intersystem crossing to the triplet state is virtually complete. There is general agreement that their lowest triplet states are of the  ${}^3n,\pi^*$  type, in which the excitation is located primarily in the carbonyl group which gives them the power to abstract hydrogen atoms from other molecules.\* In agreement with this, it has been shown that in pure benzaldehyde the reaction of a benzaldehyde molecule in the excited triplet state and one in the ground state, that is, the same reaction as (2) in the reaction scheme, occurs with a quantum efficiency of 1.<sup>2</sup>

There can be no doubt, therefore, that the first of the conditions, upon which the reaction scheme is founded, is fulfilled. As regards the second condition, the results evidently cannot be explained on the basis of spontaneous deactivation of the triplet to the ground state, competing with reactions (1)

\* For a recent review, see Wagner and Hammond.<sup>10</sup> The particular case of benzaldehyde has been discussed by Bäckström and Riiner.<sup>2</sup>

and (2). Its lowering effect on  $a(\text{H}_2\text{O}_2)$  would decrease with increasing aldehyde concentration and, above all, it would be considerably less in the more reactive of the two alcohols, benzyl alcohol. Reaction (2) may be expected to occur at essentially the same rate in both alcohols, and the values of  $k_2/k_1$  are known. Assuming  $a(\text{H}_2\text{O}_2)$  at low aldehyde concentrations to be ca. 0.80 in 2-propanol and 0.32 in benzyl alcohol, a calculation shows that these values would indicate a 40 times higher rate of deactivation in benzyl alcohol than in 2-propanol.

What seems to be required to explain our results is a mechanism by which only a fixed fraction of the triplet benzaldehyde molecules, different for the two alcohols, are in such a state that they can undergo hydrogen abstraction reactions. We believe that this mechanism must in some way be connected with hydrogen bonding.

*Hydrogen bonding in alcohols.* Alcohols are highly associated liquids as a result of the formation of hydrogen bonds between hydroxyl groups. An exhaustive treatment of this subject is included in a monograph by Pimentel and McClellan,<sup>11</sup> to which we refer.

Our present knowledge of hydrogen bonding in alcohols is to a large extent based on data obtained from infra-red spectroscopy. At low concentrations of an alcohol in  $\text{CCl}_4$ , which is regarded as an inert solvent, the absorption spectrum in the O—H stretching region is dominated by a narrow band at ca.  $2.76 \mu$ , due to OH groups not participating in hydrogen bonds.\* Extrapolation to infinite dilution gives the molar extinction coefficient of the monomer at this wavelength, which makes it possible to calculate the fraction ( $\alpha$ ) of the alcohol present as monomer at different total alcohol concentrations. This forms the basis for the calculations that have been made for various alcohols of the equilibria:  $\text{ROH} + (\text{ROH})_n \rightleftharpoons (\text{ROH})_{n+1}$ . Of necessity, these calculations have had to be based on simplifying assumptions regarding the equilibrium constants for the formation of the various hydrogen bonded species. Mecke<sup>12</sup> assumed that these constants all had the same value for a given alcohol. Coggeshall and Saier<sup>13</sup> found that better agreement could be obtained by assuming a different value for the formation of the dimer. As regards the alcohols used in this work, the values of the constants for benzyl alcohol in  $\text{CCl}_4$  at room temperature, given by Coggeshall and Saier, indicate a value of  $\alpha$  in pure benzyl alcohol (10 M) of only 0.03. For the mean association number  $f = \bar{M}/M_1$ , where  $\bar{M}$  is the average molecular weight and  $M_1$ , that of the monomer, a value of ca. 7 is obtained. Similarly, calculations according to Mecke, based on the experimental results of Hoffmann,<sup>14</sup> indicate that at  $21.5^\circ\text{C}$   $\alpha \approx 0.03$  and  $f \approx 6$  both in pure benzyl alcohol and in 2-propanol (13 M).\*\*

At the temperature of our experiments the alcohols are undoubtedly even more highly associated than indicated by the above figures.

In crystalline alcohols the molecules are, according to Pauling,<sup>17</sup> usually combined by hydrogen bonds to polymers, where the H-bonds form zigzag chains. X-Ray evidence for chain structures in liquid alcohols has been presented. On the other hand, certain results of IR-spectroscopic investigations have been interpreted as showing that dimers and trimers may have cyclic structures.

\* The spectra of benzyl alcohol in  $\text{CCl}_4$  solution at different temperatures and concentrations are shown in Ref. 11, Fig. 3-2.

\*\* It has been shown that  $\pi$ -electron systems, such as aromatic rings, can function as weak proton acceptors in hydrogen bonding.<sup>15</sup> The similar results of the calculations for the two alcohols indicate that bonding forces of this kind are too weak compared to those between the hydroxyl groups to be of importance in benzyl alcohol. Cf. also Perrins and Simons.<sup>16</sup>

*Phosphorescence of benzaldehyde in pure alcohols at low temperatures.* In two recent papers Meyer,<sup>18</sup> and Gacoin and Meyer,<sup>19</sup> present the results of investigations of the phosphorescence at 77°K of benzaldehyde and of acetophenone in different pure solvents. These results are of the greatest interest in connection with the present work. Their experimental technique made it possible both to measure the rate of decay of the phosphorescence and to register its spectrum at different stages of the process. With vitreous ethanol as solvent the phosphorescence was in both cases found to be abnormal in two respects. The decay was non-exponential; and it was accompanied by spectral changes indicating emission from molecules in two different states with somewhat different emission spectra and decay rates. The authors point out that both these states must be of the  $^3n,\pi^*$  type. They are attributed to molecules solvated (hydrogen bonded to the alcohol<sup>18</sup>) in two different ways, the most perturbed state being the one with the longer lifetime and its emission spectrum displaced toward shorter wavelengths.

The same phenomena as in ethanol are said to have been observed in vitreous 2-propanol, although somewhat less pronounced.

If it may be assumed that also in liquid alcohols, benzaldehyde molecules may exist in a triplet state which is highly perturbed as the result of hydrogen bonding, and that in this state they are unable to react with the alcohol or with other aldehyde molecules, this would explain our low quantum yields. If they are incorporated in a polymeric alcohol complex, their inability to react might be due to steric hindrance.

This possible explanation of our results receives strong support from the low quantum yield reported by Yang *et al.*<sup>20</sup> for the photoreduction of acetophenone in liquid 2-propanol in the absence of oxygen. For the consumption of acetophenone they found a quantum yield of 0.68, corresponding to an even lower quantum yield for the primary reaction of the photo-excited ketone molecule with the alcohol.\*

We conclude that under our experimental conditions only a definite fraction  $\beta$  of the triplet excited benzaldehyde molecules formed are in a state in which they can undergo hydrogen abstraction reactions. On this basis the expressions for  $\phi(\text{O}_2)$  and for the  $a$ -values, that have previously been derived from the reaction scheme, have to be multiplied by  $\beta$  and those for the  $b$ -values by  $\sqrt{\beta}$ . The latter change is due to the fact that the concentration of radical I is changed from  $\sqrt{I/k_7}$  to  $\sqrt{\beta I/k_7}$ . At the temperature of the experiments  $\beta \simeq 0.80$  in 2-propanol and 0.32 in benzyl alcohol.

The  $b$ -values for  $\text{H}_2\text{O}_2$  and peracid. The expressions for  $b(\text{H}_2\text{O}_2)$  and  $b(\text{peracid})$  may be written:

$$\frac{b(\text{H}_2\text{O}_2)}{[\text{alcohol}]} = k_3 \sqrt{\frac{\beta}{k_7}} \left( 1 + \frac{k_4[\text{ald}]}{k_3[\text{alc}]} \right) \quad (8)$$

$$\frac{b(\text{per})}{[\text{aldehyde}]} = k_4 \sqrt{\frac{\beta}{k_7}} \left( 1 + \frac{k_6[\text{ald}]}{k_5[\text{alc}]} \right) \quad (9)$$

\* Owing to secondary reactions between the free radicals formed in the primary reaction, and unexcited ketone molecules, these two quantum yields are equal only in infinitely dilute solution. Cf. for instance Bäckström and Niklasson.<sup>21</sup>

As shown by Fig. 5, the experimental values for  $b(\text{H}_2\text{O}_2)$  in 2-propanol, when plotted as  $b(\text{H}_2\text{O}_2)/[\text{alc}]$  vs.  $[\text{ald}]/[\text{alc}]$ , give satisfactory agreement with the full-drawn straight line in the diagram. However, the equation of this line is  $b(\text{H}_2\text{O}_2)/[\text{alc}] = 2.20 \times 10^{-4}(1 + 59[\text{ald}]/[\text{alc}])$ , and therefore has a slope which is *ca.* 4 times the value of  $k_4/k_3$ . For comparison, a dashed straight line has been drawn with the same intercept but with the slope required by eqn. (8).

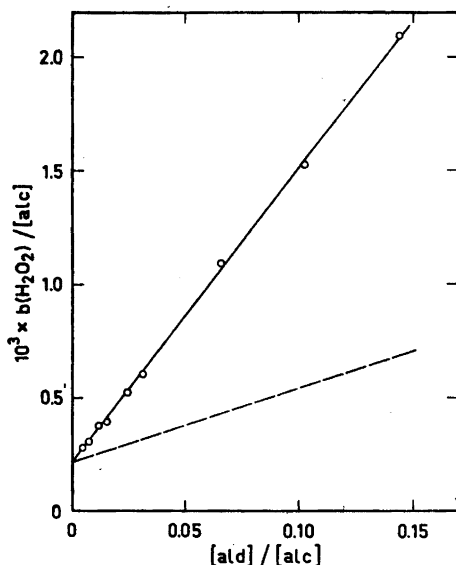


Fig. 5.  $b(\text{H}_2\text{O}_2)/[\text{alcohol}]$  vs.  $[\text{aldehyde}]/[\text{alcohol}]$  from experiments with 2-propanol. For further explanations, see text.

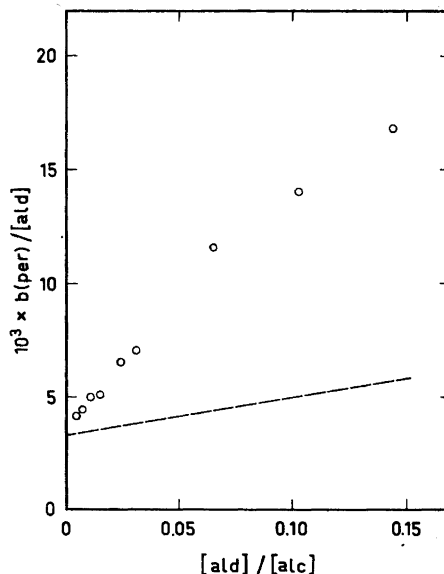


Fig. 6.  $b(\text{peracid})/[\text{aldehyde}]/[\text{alcohol}]$  vs.  $[\text{aldehyde}]/[\text{alcohol}]$  from experiments with 2-propanol. For further explanations, see text.

Fig. 6 shows similar large deviations from the reaction scheme in the case of the  $b$ -values for peracid in 2-propanol. The equation of the dashed straight line corresponding to eqn. (9) is  $b(\text{per})/[\text{ald}] = 33.0 \times 10^{-4}(1 + 5[\text{ald}]/[\text{alc}])$ . The value at  $[\text{ald}] = 0$  was obtained by multiplying the extrapolated value of  $b(\text{H}_2\text{O}_2)/[\text{alc}] = 2.20 \times 10^{-4}$  by  $k_4/k_3 = 15$ , on the assumption that the former value is  $= k_3 \sqrt{\beta/k_7}$ .

As a measure of the deviations, the ratio  $R = b(\text{observed})/b(\text{calculated})$  may be used. In Fig. 7 the values of  $R$  obtained both from the  $b(\text{H}_2\text{O}_2)$ -values and from the  $b(\text{peracid})$ -values have been plotted vs. the aldehyde concentration for both alcohols. It will be seen that the deviations are considerably larger in 2-propanol than in benzyl alcohol. The experimental points also indicate that the shapes of the  $R$ -curves are markedly different in the two cases. At a given aldehyde concentration the  $R$ -values obtained from  $b(\text{H}_2\text{O}_2)$  and  $b(\text{peracid})$  agree within limits of error. This was to be expected since the product distribution at constant  $[\text{aldehyde}]$  has been found to be independent of  $\phi(\text{O}_2)$ .

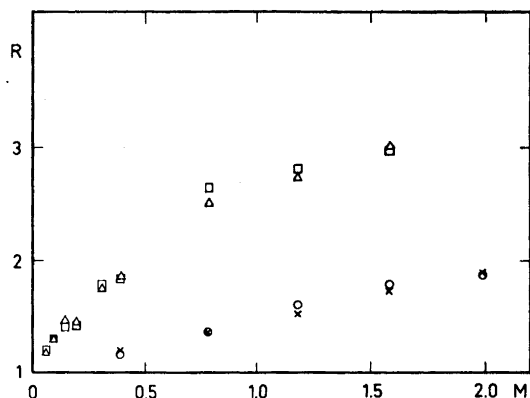


Fig. 7.  $R = b(\text{observed})/b(\text{calculated})$  vs. aldehyde concentration. In 2-propanol:  $\Delta$   $R$  from  $b(\text{H}_2\text{O}_2)$ ;  $\square$   $R$  from  $b(\text{peracid})$ . In benzyl alcohol:  $\circ$   $R$  from  $b(\text{H}_2\text{O}_2)$ ;  $\times$   $R$  from  $b(\text{peracid})$ .

The only explanation of our results that we have been able to think of rests on the assumption, that radical I may form a complex with a molecule of benzaldehyde:  $\text{I} + \text{aldehyde} \rightleftharpoons \text{complex}$ ;  $[\text{complex}] = K \times [\text{I}][\text{aldehyde}]$ . In the complex the radical must, of course, be bound in such a way that it is prevented from reacting with the aldehyde molecule in the normal way by hydrogen abstraction. This does not seem impossible in view of the fact that both the aldehyde molecule and the radical are undoubtedly hydrogen-bonded to the alcohol, the oxygen atom of the carbonyl group and those of the peroxy group acting as proton acceptors. The aldehyde-bonded radical must be able to react in the same way as "free" radicals, although presumably with lower values of the rate constants, particularly those of the two possible chain-breaking reactions corresponding to reaction (7). Preliminary calculations have indicated that the results may be accounted for on this basis if reasonable assumptions are made with regard to the reactivity of the aldehyde-bonded radical I compared to that of the "free" radical.

This problem will be discussed further in a subsequent paper by C. Åquist.

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#### REFERENCES

1. Bäckström, H. L. *J. Z. physik. Chem. (Leipzig)* **B 25** (1934) 99.
2. Bäckström, H. L. J. and Riiner, U. *Acta Chem. Scand.* **20** (1966) 630.
3. Calvert, J. G. and Pitts, Jr., J. N. *Photochemistry*, Wiley, New York 1966, pp. 703—705 and 783—786.
4. Berntsson, S. *Anal. Chem.* **28** (1956) 2337.
5. Debais, L., Niclause, M. and Letort, M. *J. Chim. Phys.* **56** (1956) 41.
6. D'Ans, J., Mattner, J. and Busse, W. *Angew. Chem.* **65** (1953) 57.
7. Schenck, G. O. and Becker, H.-D. *Angew. Chem.* **70** (1958) 504.
8. Bäckström, H. L. *J. The Svedberg 1884—1944*, Almqvist & Wiksells Boktryckeri, Uppsala 1944, p. 45.

9. Kasha, M. *Discussions Faraday Soc.* **9** (1950) 14.
10. Wagner, P. J. and Hammond, G. S. *Advan. Photochem.* **5** (1968) 21.
11. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*, W. H. Freeman Co., San Francisco 1959.
12. Mecke, R. *Discussions Faraday Soc.* **6** (1950) 161.
13. Coggeshall, N. D. and Saier, E. L. *J. Am. Chem. Soc.* **73** (1951) 5414.
14. Hoffman, E. G. *Z. physik. Chem. (Leipzig)* **B 53** (1943) 211.
15. Schleyer, P. von R., Wintner, C., Trifan, D. S. and Bacskai, R. *Tetrahedron Letters* **1959** No. 14, 1.
16. Perrins, N. C. and Simons, J. P. *Trans. Faraday Soc.* **65** (1969) 390.
17. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell Univ. Press, Ithaca, N.Y. 1960.
18. Meyer, Y. *Compt. Rend.* **B 266** (1968) 178.
19. Gacoin, P. and Meyer, Y. *Compt. Rend.* **267** (1968) 149.
20. Yang, N. C., McClure, D. S., Murov, S. L., Houser, J. J. and Dusenberg, R. *J. Am. Chem. Soc.* **89** (1967) 5466.
21. Bäckström, H. L. J. and Niklasson, R. J. V. *Acta Chem. Scand.* **22** (1968) 2589.

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