THE PHOTOCHEMICAL OXIDATION OF ORGANIC HYDROCARBONS.

Part II. Toluene, and the Oxidation of Benzaldehyde.

By C. J. Kothari and H. E. Watson.

In the first part of this series (Sudborough, Watson and Narayanan, *J. Indian Inst. Sci.*, 1925, 8A, 1) an account was given of preliminary experiments on the oxidation of toluene by oxygen under the action of ultraviolet light in presence of anthraquinone as a catalyst. Further experiments have now been conducted with toluene, and as benzaldehyde was found to be one of the products of oxidation, an investigation has been made of the oxidation of benzaldehyde alone and in solution. It has been shown that the reactions are complex, and since the experimental difficulties of uniformly exposing solutions to the action of a gas are considerable, and the velocity is influenced by minute traces of impurities, it has been difficult to obtain strictly quantitative values in all the experiments. Several facts have however been brought to light, and further work on the subject being postponed, it appears desirable to record the results so far obtained. Before the mechanism of the reactions can be elucidated much more detailed work will be required.

TOLUENE.

References to previous work upon toluene have already been given in part I. To these may be added a short paper by John (*Ber.*, 1925, 58, 1563), in which it was shown that the rate of formation of benzoic acid in sunlight with anthraquinone as catalyst depended upon the elevation above sea-level, evidently owing to the increased amount of ultraviolet light at higher altitudes.

EXPERIMENTAL.

The general arrangements were the same as those described in part I, the reaction mixture being placed in a closed distilling flask connected with an oxygen reservoir and shaken in close proximity to a mercury arc lamp. The products were analysed for benzoic acid as before and in addition, a more detailed examination according to the method of Eckert (*Ber.*, 1925, 58, 1563) was made to detect other substances which might have been formed in the reaction. Benzaldehyde and a substance which appeared to be isohydrobenzoin were isolated but hydrobenzoin, benzil and dibenzyl found by Eckert could not be identified. Kailan (*Monatsh.*, 1919, **40**, 445) mentions formic and oxalic acids as reaction products, the former occurring in the aqueous layer in a quantity approaching that of the benzoic acid, but his deductions were based mainly on conductivity measurements and in neither case does he appear to have isolated the acid or a derivative; he states, however, that the solution reduced ammoniacal silver nitrate solutions. In our experiments no solution was obtained exhibiting this property but on the other hand the aqueous liquors gave the usual tests for hydrogen peroxide. In addition, the amount of permanganate decolorised by the solution corresponded with a quantity of formic acid much greater than the total acidity of the solution, which was mainly due to benzoic acid. The presence of hydrogen peroxide therefore seems highly probable and its formation may account for the greater rates of oxidation observed in presence of a large proportion of water; Kailan, reasoning from experiments in the absence of toluene, considered the formation of hydrogen peroxide unlikely. It is possible that both series of observations are correct since Kailan's experiments were made without a catalyst and the mechanism of the reaction may be different in the two cases.

Preliminary experiments showed that a mixture of toluene, anthraquinone and water underwent no appreciable oxidation in the dark in 3 months at room temperature or in 133 hours at 60°. Illumination with a 1 kilowatt metal filament lamp was also without effect. On the other hand, reaction was found to proceed at very nearly equal rates in quartz and glass vessels under the influence of the radiation from a quartz mercury arc lamp, a fact previously noted by John (*loc. cit.*). The later experiments were consequently conducted in glass vessels.

The Course of the Reaction.

Three flasks each containing 50 g. toluene, 5 g. water and 2·5 g. anthraquinone were exposed simultaneously to light from the arc at a distance of about 15 cm. with continuous shaking, a slight positive pressure of oxygen being maintained. The experiment was stopped during the night and at the end of each day's run; after cooling and allowing the mixture to separate into two layers, 5 c.c. of the toluene solution were withdrawn from one of the flasks and titrated. When the contents of one flask were exhausted samples were taken from the next. Table I shows the total quantity of benzoic acid in the toluene layer at the end of each day's exposure and the number of milligrams of acid produced per hour for the corresponding period.

TABLE I.

Rate of formation of benzoic acid from toluene.

FLASK 1.			FLASK 2.			FLASK 3.		
Time hours	Total acid g.	mg./hr.	Time hrs.	Total acid g.	mg./hr.	Time hrs.	Total acid g.	mg./hr.
9·7	0·014	1·4	62	0·71	(11)	111	2·00	(18)
16·0	0·020	1·1	69	0·84	27	118	1·81	21
22·3	0·026	1·6	76	0·95	27	125	1·78	23
28·3	0·034	2·5	83	1·00	21	132	1·73	23
35·0	0·052	4·3	90	0·92	23	139	1·67	24
41·7	0·066	3·7	97	0·93	21	146	1·55	20
49·2	0·080	4·4	104	0·86	14	153	1·40	19
...	...	...	111	0·77	14	...	...	...
Total acid formed	0·163	...	...	1·75	...	...	3·22	...

These figures show that initially the reaction is very slow but the rate increases steadily and tends to approach a constant value. Flask 2 was a little closer to the light than flask 3 and this may partly account for the somewhat higher rate in the former case when the contents were first examined. As the volume of toluene was diminished by withdrawing samples, the rate of acid-formation fell, an effect best seen with flask 2. The quantity of acid in flask 2 at the end of 62 hours is evidently much greater than the total amount which would have been formed in flask 1 if the reaction had been allowed to continue another 13 hours and the quantity in flask 3 after 111 hours exposure is greater than the total amount formed in flask 2 in this period. The explanation is that the reaction does not take place solely at the glass surface as appears to be the case with benzaldehyde ; but that oxidation occurs throughout the liquid and depends on the total volume. As water is always present, it is probable that the extent of the water-toluene interface is the controlling factor. It may be mentioned that the 'total acid' given in the table is the sum of the acid in the flask and the quantity removed as samples. In some cases the sample contains more acid than is formed during the subsequent period of exposure so that the amount in the flask diminishes.

After 153 hours' exposure, 40 c.c. of fresh toluene and the corresponding quantity of anthraquinone were added to 13 c.c. of toluene and the water from flask 3, and the exposure was continued. The rate of acid formation was only 6 mg./hr. for the first 7 hours increasing to 10 and 12 mg. for the next two similar periods. This rate is much greater than the initial figures for flask 1 and renders it improbable that the slow oxidation when the reaction is first started is due to an anticatalyst contained in the toluene which is slowly destroyed. It appears more likely that intermediate products are formed and thus, on dilution, the rate is lowered until they again attain their maximum concentration. The possibility of benzaldehyde being such an intermediate product was tested by adding 0·3 c.c. to a fresh reaction mixture, but no initial acceleration was observed; in another experiment, the residue left in a flask which had been exposed to light for a prolonged period and from which the toluene had been distilled was added to fresh toluene, also without any result. It follows therefore that the accelerator is either readily volatile or is destroyed by heat. A peroxide would satisfy these conditions.

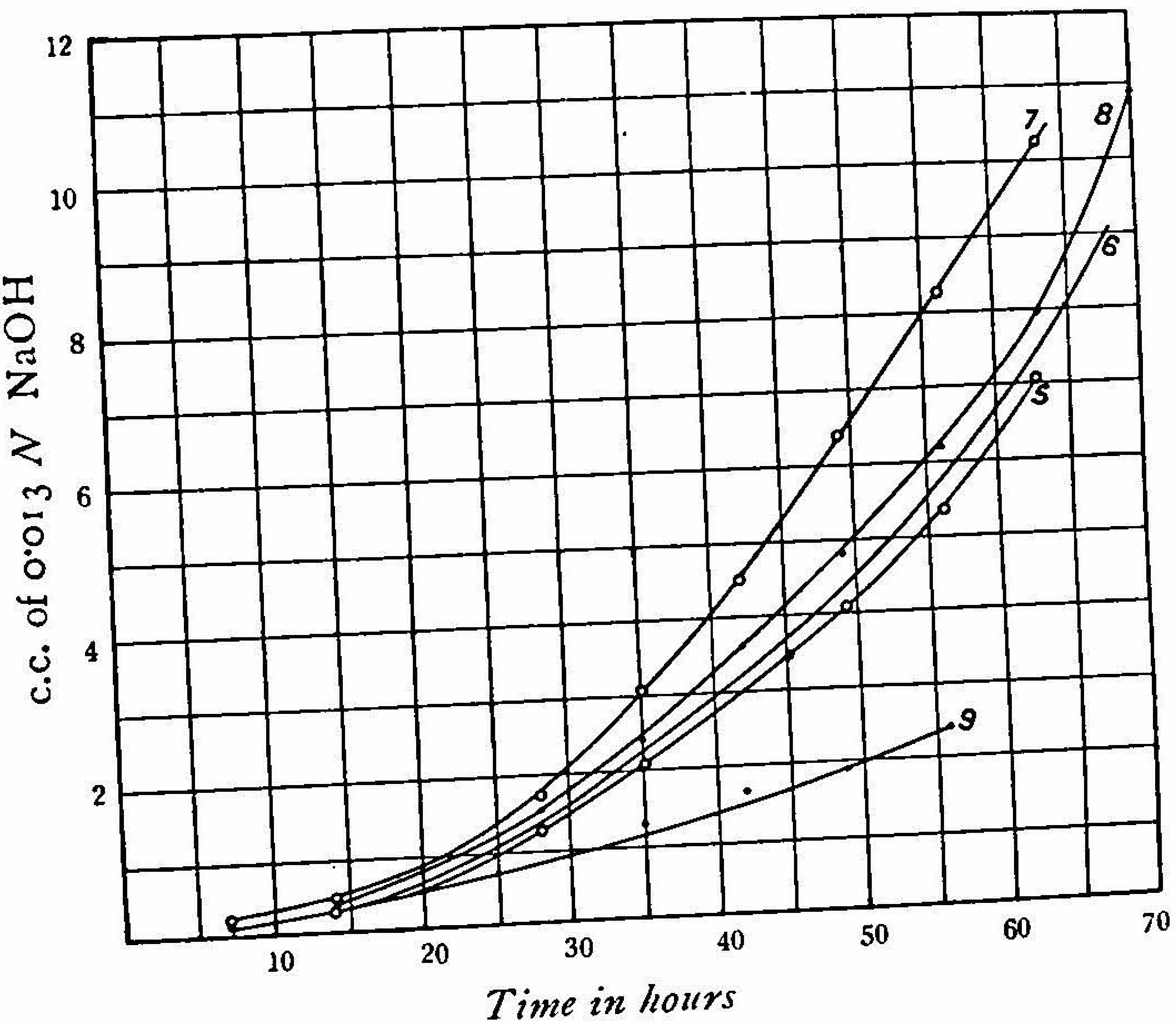
The fall in reaction-rate may be partly due to the accumulation of benzoic acid. To examine this possibility, an experiment similar to the preceding was conducted and the concentration of acid determined at regular intervals. After 80 hours' exposure, when the concentration was 3 g. in 100 c.c., the benzoic acid was removed by extraction with sodium carbonate and the mixture again exposed. The curve connecting the rate of increase of concentration with time showed no discontinuity, indicating that at the concentration examined the effect was negligible.

The previous experiments were made with 5 per cent. of catalyst, the quantity recommended by Eckert. As this proportion was not completely soluble it appeared likely that a smaller amount would be equally efficacious, and so a series of experiments was conducted in which varying proportions of anthraquinone were added to a mixture of 50 g. of toluene and 5 c.c. of water. The results expressed as c.c. of 0·013 *N* sodium hydrate required to neutralise 5 c.c. of the solution are shown in fig. I, all samples being withdrawn at equal intervals. The percentage of catalyst used in experiments 5 to 9 was 4·3, 2·5, 1·0, 0·5 and 0·05, respectively. The most rapid formation of acid is with 1 per cent. of catalyst. This stage in the experiments was reached in the early part of the year, the period of minimum cloudiness and the opportunity was taken to make some measurements in sunlight.

Oxidation by Exposure to Sunlight.

The method adopted was the same as with the mercury arc, the whole apparatus being placed out of doors in an exposed position. The usual temperature attained was about 50°, somewhat lower than in the case of the arc.

FIG. I.


12
10
8
6
4
2
c.c. of 0·013 N NaOH
10
20
30
40
50
60
70
Time in hours
7
8
6
5
9

The effect of adding quinones and uranium salts, which are known to act as photo-catalysts in some reactions, was first tried. It has already been shown by Benrath and Meyer (*Ber.*, 1912, **45**, 2707) that phenanthraquinone accelerates the oxidation of toluene, but becomes oxidised to diphenic acid and hence cannot be used for long periods. No experiments appear to have been made with other quinones except anthraquinone and consequently we have tried benzoquinone and camphorquinone. The former was found to decompose rapidly yielding a dark solution in about 30 minutes, while the latter substance also changed, the originally yellow solution becoming colourless in 3 to 4 hours.

Table II shows the c. c. of 0·1 *N* sodium hydrate solution required to neutralise a mixture of 25 g. toluene and 12·5 g. water after exposure. The weight of catalyst in expts. 1 and 2 was 0·5 g., and in expt. 3, 0·3 g.

TABLE II.

Expt. No.	Exposure hours	c. c. 0·1 *N* NaOH for whole mixture		
		Uranium nitrate	Uranium acetate	Anthraquinone
1	24	21·3	30·1	80·2
2	47	26·9	23·7	226·0
		Benzoquinone	Camphorquinone	
3	70	5·8	19·2	266·4

The experiments were conducted at different times and are thus not comparable with each other owing to variations in the light intensity. The uranium salts have some catalytic action, but the results are irregular and the amount of oxidation does not appear to increase with the time. Benzoquinone and camphorquinone as anticipated give rise to very little oxidation, the acid being in all probability formed for the most part by direct reduction of the catalyst. Hydrogen peroxide was not detected in any of the solutions except when anthraquinone was used, pointing to difference in the mechanism of oxidation.

The proportion of toluene oxidised in these experiments when anthraquinone was used as catalyst (8·3 and 9·8 per cent. in experiments 2 and 3, respectively) was larger in proportion to the time than in any of those with a mercury arc as the source of light. For example, in the preliminary experiments with quartz flasks, 12·2 per cent. was converted in 200 hours and in experiments recorded later the amounts in 70 hours were 2·6 and 4·3 per cent. In these only 10 per cent. of water was used. In the previous series of experiments with 25 per cent. of water the highest value in 200 hours was 11·6 per cent.

Although experiments had shown that small quantities of benzaldehyde did not influence the rate of reaction, this fact would not disprove its formation as an intermediate product in the scheme,

Toluene → benzaldehyde → benzoic acid.

If this were the case, pyrogallol, which is an inhibitor of the second reaction, should reduce the rate of formation of benzoic acid from toluene. To test this hypothesis three solutions were made each containing 25 g. toluene, 12·5 g. water and 0·3 g. anthraquinone; pyrogallol was added to two, and all three were exposed simultaneously to sunlight for 34 hours with continuous shaking. The acid formed was then titrated with 0·1 *N* sodium hydroxide solution with the following results :—

Pyrogallol, g.	...	0·0	0·005	0·01
c. c. 0·1 *N* NaOH	...	136	148	155

It appears from these figures that pyrogallol, instead of retarding the reaction, slightly accelerates it and consequently the suggested mechanism with benzaldehyde as an intermediate product is probably incorrect unless the rate of oxidation of benzaldehyde is so great that even in presence of pyrogallol it is large compared with the rate of oxidation of toluene.

It is unfortunately not easy to study the oxidation of very dilute solutions of benzaldehyde and so an examination of the reaction under other conditions has been made. This has shown that toluene itself exerts a retarding influence, thereby introducing a further complication, and so far, it has not been possible to arrive at a definite conclusion.

THE OXIDATION OF BENZALDEHYDE.

The oxidation of benzaldehyde by oxygen has been studied by Schönbein (*J. pr. Chem.*, 1858, **74**, 328; 1861, **84**, 406; 1868, **105**, 226), Bach (*Compt. rend.*, 1897, **124**, 951) who showed the presence of peroxides in the oxidised mixture, Engler and Wild (*Ber.*, 1897, **30**, 1677), and Nef (*Annalen*, 1897, **298**, 280) who were of opinion that benzoyl peroxide in addition to hydrogen peroxide was present, Staudinger (*Ber.*, 1913, **46**, 3530) and more recently by Jorrisen and his collaborators (*Rec. trav. chim.*, 1926, **45**, 245; 1927, **46**, 42). These authors actually isolated from the reaction products the benzoyl hydroperoxide, $C_6H_5 \cdot CO \cdot O \cdot OH$, prepared by Baeyer and Villiger (*Ber.*, 1900, **33**, 1582), but later found that the course of the reaction depended upon the solvent. Kailan (*Monatsh.*, 1912, **33**, 1305) measured the reaction velocity in solutions of benzene and alcohol under the influence of light from a quartz mercury arc, and found the temperature coefficient to be small.

Moureu and Dufraisse (*Compt. rend.*, 1922, **174**, 258; 1924, **178**, 824, 1861; 1924, **179**, 237; 1926, **183**, 408) have made a careful study of the action of inhibitors in very weak light and have explained it by supposing the formation of peroxides which mutually destroy each other, regenerating the original compounds.

While the present work was in progress an important contribution was made to the subject by Reiff, (*J. Amer. Chem. Soc.*, 1926, **48**, 2893) who showed the part played by the surfaces with which the aldehyde was in contact, particularly when they were wet. Still more recently Backstrom (*J. Amer. Chem. Soc.*, 1927, **49**, 1460) has made measurements of the quantum efficiency and deduced that the photochemical reaction is a chain reaction; moreover, because inhibitors have a similar action on both thermal and photochemical reactions, he concludes that the former is a chain reaction as well. Unfortunately his inhibitors did not include those which have been most commonly studied. None of these papers can be said to afford conclusive evidence regarding the reaction and our experiments tend to show that a number of factors must be taken into account.

EXPERIMENTAL.

Benzaldehyde was distilled under reduced pressure and stored in the dark in small sealed tubes. The early experiments were made with a sample which was subsequently found to contain chlorine compounds; later this was replaced by a chlorine-free product made from toluene. The benzene and toluene used as solvents were carefully purified.

Preliminary experiments made by bubbling oxygen through a 33 per cent. solution of benzaldehyde in toluene and measuring the amount absorbed showed that the reaction took place in the dark and had an appreciable temperature-coefficient; it was also retarded if the solution is in contact with rubber. The results were irregular and it was evident that careful control of temperature and a fixed rate of bubbling were essential if consistent values were to be obtained. Immersion of the reaction vessel in a thermostat was found unsatisfactory as it was difficult to keep the water perfectly clean. The gas circulating devices of Pearson and Thomas (*J.C.S.*, 1925, **127**, 2450) and of Chatterji and Finch (*J.C.S.*, 1925, **127**, 2464) were tried but did not satisfy the requirements of these experiments. The arrangement finally employed is shown in fig. II. A 50 c.c. jacketed gas burette *A*, was used to hold a supply of oxygen and measure its volume. The gas was passed through the reaction vessel *B* by means of a circulating pump consisting of two mercury reservoirs *CC* connected by rubber tubing, one of which could be raised and lowered at constant intervals by means of an eccentric attached to gearing driven by a motor. The valves *DD* consisted of globules of mercury at the junction between a capillary and a wider tube. Gas could bubble through the mercury in one direction but was prevented from passing the other way by the rise of the mercury in the capillary tube. These valves were very satisfactory and did not leak. The delivery of the pump could be varied by changing the lift or altering the rate. As used, at 20 revolutions per minute the volume of gas circulated was 2 litres per hour. The water in the gas burette formed a buffer tending to equalise pressure variations and the result was a nearly steady stream of gas through the reaction liquid. The reaction vessel *E* was immersed in a vessel of distilled water with flat sides, the temperature being maintained constant by a coil through which was circulated water from a thermostat. For illumination, a 100 c.p. pointolite lamp run with a constant current of 1·2 amps. at a distance of 19 cm. from the reaction vessel was used, the light passing through a filter containing water to cut off the heat rays.

When starting an experiment the apparatus was first filled with oxygen from a gas holder and the air displaced. Gas was then admitted to the gas burette and the circulating pump started. At 20 or 30 minute intervals it was stopped and the volume read; when the gas burette was empty fresh oxygen was introduced from the gas holder. This sometimes caused an irregularity in the next reading particularly with benzene as solvent owing to the fresh gas not being saturated with the vapour. It was found that if the gas was bubbled through the solvent before admission the irregularity was minimised although not always entirely eliminated.

Preliminary experiments showed that the rate of absorption of oxygen fell in an unexpected manner as the reaction progressed and it was suspected that the benzoic acid produced by the reaction might have an inhibiting effect. Several observations were made for solutions containing benzoic acid and the results are shown in table III which gives the volume of oxygen (c.c. at N.T.P.) absorbed in successive periods of 30 minutes by a toluene solution containing 33 per cent. of aldehyde.

FIG. II.

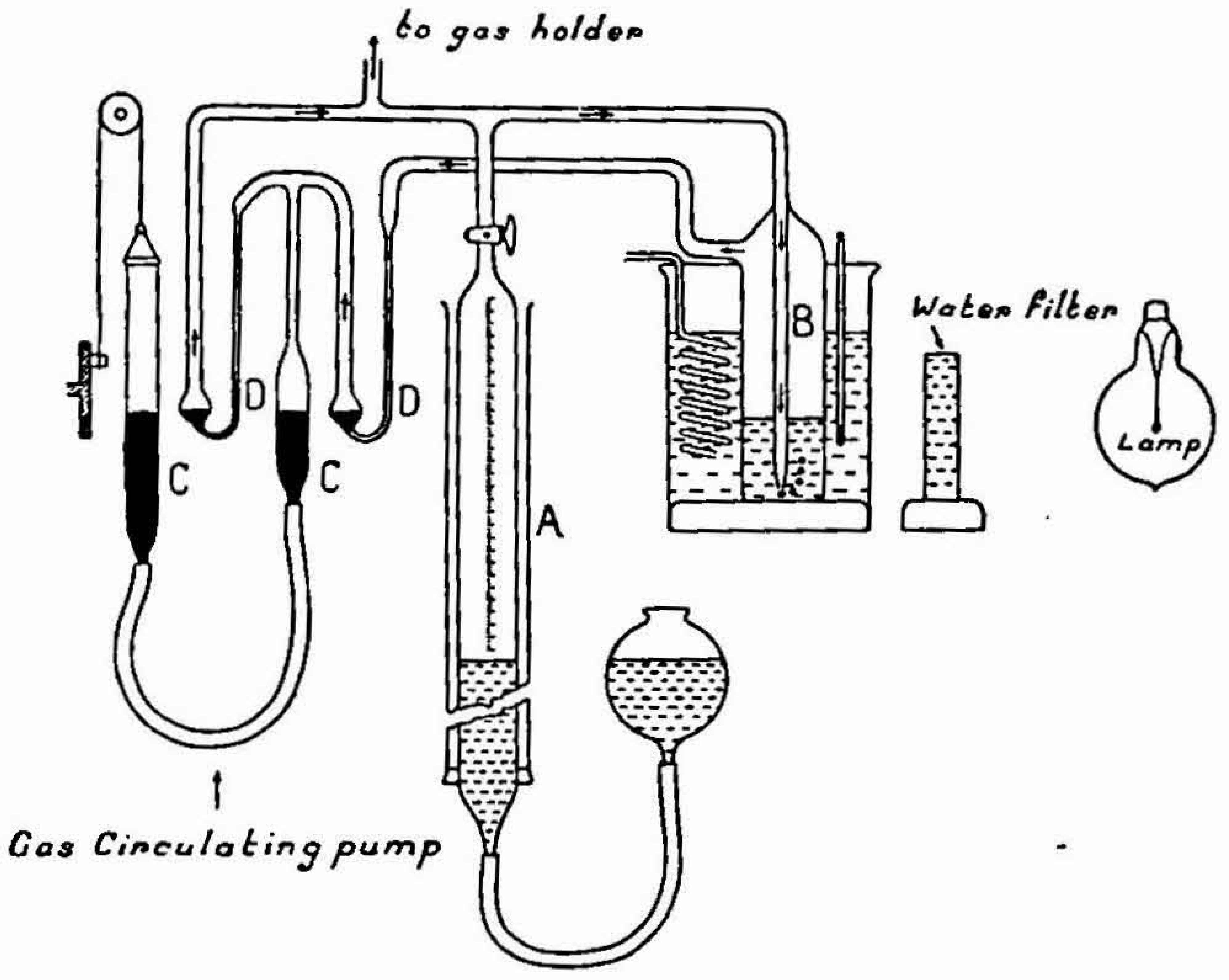

to gas holder
Water filter
B
Lamp
D
D
C
C
A
Gas Circulating pump

TABLE III.

Absorption of oxygen in 30 minutes by 33 per cent. solution of benzaldehyde in toluene.

Expt. No. 16	18	20	27
No acid	0·9 g. acid I	0·9 g. acid II	0·9 g. acid III
15·1	22·7	14·9	17·8
15·1	17·5	13·9	18·0
14·9	14·4	11·0	14·9
12·0	12·3	9·7	11·3
12·1	10·5	8·2	9·8
11·4	10·0	7·5	9·3
10·2	10·0	7·3	8·6
10·0	9·0	6·5	...
100·8	106·4	79·0	...

The quantity of acid formed at the end of expt. 16 was approximately 0·9 g. and this amount was added in each of the other three experiments. If the acid had a retarding effect, the initial rate of absorption in these should have been the same as the final rate in expt. 16, but this was not so. Acid I was a fairly pure commercial acid and its effect was to accelerate the reaction initially although the relative retardation occurring subsequently was greater than in expt. 16. Acid II was recovered from previous oxidation experiments and in its presence the rate was definitely retarded, particularly in the later stages. Acid III was a specially purified sample prepared from toluene.

These results might be explained by the assumption that the benzoic acid used in expts. 18 and 27 and the benzaldehyde itself, contained as impurity an accelerator which was gradually destroyed as the reaction proceeded. Subsequent experiments, however, have failed to confirm this hypothesis. A comparison of expts. 16 and 20 indicates that pure benzoic acid has a retarding influence especially at higher concentrations, but it is evident that the rapid fall in reaction velocity is not due solely to the accumulation of the reaction product.

The sample of benzaldehyde used in the experiments just described as well as the first two samples of benzoic acid were found to contain traces of chlorine. It was therefore decided to try the effect of adding to a chlorine-free specimen of benzaldehyde small quantities of such chlorine compounds as might occur as impurities. Table IV shows the quantities of oxygen absorbed in successive periods of 30 minutes by a 50 per cent. solution of benzaldehyde in toluene at 30° with different additions, the illumination and rate of bubbling being as before.

TABLE IV.

Absorption of oxygen in 30 minutes by 50 per cent. solution of benzaldehyde in toluene.

Expt. No.	Substance	Oxygen absorbed						Total, 3 hours
12	Benzaldehyde impure ...	57·9	49·3	41·7	35·0	31·5	24·5	239·9
4	Benzaldehyde pure (*a*) ...	47·0	42·1	36·2	27·6	26·5	22·4	201·8
5	*do.* + 0·05 g. *o*-chlorobenzoic acid ...	50·2	41·1	32·7	28·4	25·5	22·1	200·0
7	*do.* + 0·05 g. *m*-chlorobenzoic acid ...	45·6	51·3	43·7	38·7	28·9	25·0	233·2
8	*do.* + *do* *do.* ...	42·3	53·2	44·7	32·4	26·9	22·0	221·5
10	*do.* + 0·02 g. *p*-chlorobenzoic acid ...	44·2	38·6	32·2	28·5	26·0	22·2	191·7
17	Benzaldehyde pure (*b*) ...	43·7	39·0	31·1	26·5	24·2	20·7	185·2
16	*do.* + 0·1 g. benzyl chloride ...	35·1	30·8	28·8	25·2	21·0	19·5	160·4
18	*do.* + 0·05 g. *do.* ..	42·1	35·5	30·3	27·0	...	...	...
21	*do.* + 0·2 g. benzyl chloride ...	36·3	31·3	25·6	21·3	14·1	15·0	143·6
20	*do.* + 0·1 g. *do.* ...	38·6	30·2	23·5	21·0	19·5	17·9	150·7
23	*do.* + 0·2 g. benzotrichloride...	32·2	27·5	25·0	23·4	18·0	14·0	140·1
24	*do.* + 0·02 g. *do.* ...	48·3	34·3	32·4	28·6	27·3	27·3	198·2
30	*do.* + 0·1 g. anthraquinone ...	61·6	49·2	45·1	40·6	37·5	33·2	267·2

Examination of these figures reveals the fact that in spite of all precautions, the rate of oxidation is irregular and the experimental error large; consequently too much reliance must not be placed upon individual results. Certain conclusions can, however, be drawn and of these the most obvious is the diminution in the rate of absorption to approximately half its original value in 3 hours, the decrease in concentration for the absorption of 200. c. c. being only 16 per cent. It will be shown later that the rate of oxidation diminishes much more rapidly with decrease in concentration than it would if it were directly proportional to the concentration, so that the observed decrease in rate is largely a concentration effect.

The absorption of the impure benzaldehyde used in the previous experiments was greater than that of any admixture with the chlorine compounds tested and was only exceeded when anthraquinone was added. The two pure samples (*a*) and (*b*) were from the same source, but (*b*) had been kept for 20 days after distillation. *m*-Chlorobenzoic acid appears to have a definite accelerating influence and it is rather remarkable that the effect is most evident during the second half hour of oxidation. The results for the other chlorine compounds indicate a slight retardation and it is therefore unlikely that these cause the activity of the impure benzaldehyde. Anthraquinone increases the reaction-rate very considerably as might be expected from its effect on pure toluene. In addition to those enumerated above, a few experiments were conducted in which benzoin and benzil were added to the benzaldehyde, but no acceleration was observed.

Effect of concentration upon reaction-velocity.

Numerous determinations of the rate of oxygen absorption in toluene solutions containing various proportions of benzaldehyde were made but results even more irregular than those shown in table I were obtained. A complete duplicate apparatus was erected in order that identical solutions could be exposed to light simultaneously. Even when this was done the results were not concordant and the source of the error could not be ascertained. As work on the subject has had to be discontinued, some typical results are given in table V illustrating the general nature of the effect of concentration. All solutions were made up by volume, i.e., a 25 per cent. solution is a mixture of 25 c.c. of benzaldehyde and 75 c.c. of toluene, the exposure being at a distance of 19 cm. from a pointolite lamp consuming 1·2 amps.

The first four experiments A–D formed part of an earlier series in which the absorption tube was immersed directly in a thermostat and consequently the conditions were not quite the same as later, when the duplicate indirectly heated apparatus was used; but it will be seen

TABLE V.

Absorption of oxygen by toluene solutions of benzaldehyde, 31°.

Time h.m.	Volume percentage of Benzaldehyde																	
	25	37·5	50	62·5	40		50					60			70	75	90	100
	A	B	C	D	14B	16B	4A	22B	28B	35B	21B	7A	14A	16A	7B	5A	5B	4B
20	3·5	13·4	31·0	42·5	15·7	15·1	30·5	30·0	32·3	33·9	30·1	37·1	37·8	34·6	40·2	34·0	32·7	31·0
40	4·2	13·0	28·0	37·5	17·3	17·4	34·2	31·5	33·4	38·3	34·6	37·8	38·1	35·6	41·2	29·7	29·5	33·1
1 0	4·8	12·9	26·0	30·5	17·7	16·1	34·7	32·4	32·3	39·7	40·0	38·7	36·5	34·4	41·0	27·7	29·1	31·3
1 20	5·0	11·7	22·0	26·0	18·9	17·4	31·9	29·7	35·8	38·6	43·9	38·1	36·9	33·4	40·0	29·3	29·7	32·4
1 40	4·8	11·3	20·2	24·3	17·1	15·8	29·4	26·8	34·4	39·0	44·9	34·9	34·0	33·5	38·4	30·0	29·6	31·5
2 0	4·5	10·7	18·0	22·0	15·8	16·1	24·5	21·1	29·7	38·3	38·4	33·5	30·4	30·4	36·6	28·6	29·8	32·1
2 20	4·1	9·4	17·2	19·0	14·2	13·4	20·1	17·8	25·3	33·1	44·8	31·2	29·1	27·6	34·7	27·4	29·2	30·6
2 40	3·8	9·2	16·1	17·3	13·1	11·9	18·2	17·0	19·6	25·7	32·4	27·8	26·8	25·8	33·3	27·5	28·5	29·9
3 0	3·7	8·6	15·1	16·5	13·1	10·2	17·3	15·4	15·9			26·3	25·1	23·3	29·4	27·9	27·7	28·2
3 20	3·7	8·0	13·6	16·3	10·2	9·9	16·3	15·0	15·2			24·7	20·9	21·7		26·6	28·1	29·0
3 40	3·6	8·0	13·3	16·4														
4 0	3·5	8·0	13·0	16·4														

that the initial rates for the 50 per cent. solutions are similar. In expts. B, C and D, the oxygen absorption rate fell steadily from the beginning; in several others it increased to a maximum at the end of about an hour and then diminished. After about two hours the rate appears to depend upon the concentration of the benzaldehyde, but the relation is barely more than qualitative. For example, in expt. C the oxygen absorbed in the interval 2 h. 40 m. to 3 h. was 15·1 c.c., and the benzaldehyde concentration at the end of the period was by calculation 40·8 per cent., agreeing approximately with the initial figures for expt. 16 B. The corresponding figures in expt. 4 A were however, 17·3 c.c. for a concentration of 38·7 per cent. and the rate was thus greater while the concentration was less. In expt. 14 A the oxygen absorption measured at the end of two hours was 30·4 c.c. and the concentration 50 per cent. agreeing with expt. 4 A, while in expt. 7 B after the same time, the absorption 36·6 c.c. and concentration 59 per cent. agree approximately with the initial figures for the latter concentration.

The general relation between velocity and concentration was complex. On drawing a curve connecting the average values it was found that the velocity increased slowly at first with increasing concentration; between 30 and 60 per cent. there was a very rapid rise to a maximum at about 70 per cent. and above this figure the rate fell nearly to the value for 50 per cent. solutions. If concentration were the main factor determining the rate, it would be expected that the figures for the 75 per cent. solution would have shown a considerable increase as the reaction progressed and the concentration was reduced to 70 per cent., but this was not the case. At the same time it is to be noted that the diminution in rate was much less for the highly concentrated solutions than for the 50 per cent. solutions and this is very probably due to the comparatively small change of velocity with concentration in the former case.

Expt. 21 B is given as an example of an abnormal reaction which proceeded very rapidly at an increasing rate until crystallisation set in after 2 h. 40 m. Crystal formation was usually observed when 310–320 c.c. of oxygen had been absorbed in the case of the 50 per cent. solutions, and 330–345 c.c. in the case of the more concentrated, the time varying from 3 to 5 hours.

Reactions in benzene solution.

As toluene itself is acted upon by light it appeared desirable to examine the reaction in a simpler solvent and some experiments were consequently conducted in benzene solution. Unfortunately it was not possible to complete the examination of solutions of different concentrations, but it was found that results with benzene were less irregular than those with toluene. Table VI shows the oxygen absorption of 50 and 75 per cent. solutions compared with that of a sample of the same benzaldehyde with no solvent.

TABLE VI.

Absorption of oxygen by benzene solutions of benzaldehyde, 30·7°.

Time h. m.	Volume percentage of benzaldehyde		
	50	75	100
20	38·8	35·8	29·1
40	38·4	34·5	28·6
1 0	36·7	31·7	28·1
1 20	37·7 *	36·2 *	27·0
1 40	34·9	33·3	27·9 *
2 0	32·6	34·3	27·4
2 20	33·4 *	30·9	26·6

The values marked with a star were taken after the admission of fresh oxygen to the apparatus and cannot be regarded as reliable.

It will be seen that the course of the reaction differs in some respects from that in toluene solutions; the fall in rate of oxidation of the 50 per cent. solutions, is not so great when benzene is used as a solvent and no maximum rate is reached. The rate of oxidation of pure benzaldehyde is in both cases less than when a solvent is present, but with benzene the 50 per cent. solution is much more readily oxidised than the plain aldehyde, whereas in toluene the initial rates are similar. It is intended to examine more dilute solutions on a future occasion.

The effect of quinones.

Since anthraquinone has a marked accelerating influence upon the oxidation of toluene, as shown earlier in this paper, some experiments were conducted in which different quinones were added to benzaldehyde solutions. The volumes of oxygen at N.T.P. absorbed in successive periods of 20 minutes are shown in table VII.

In all the experiments except the first two, benzene was used as solvent. It will be observed in toluene solution anthraquinone acts as an accelerator whereas in benzene it does not, but the reaction

TABLE VII.

Absorption of oxygen in presence of quinones; 20 c.c. of 50 per cent. solution, 30·1°.

Expt. No.	Substance	Oxygen absorption								
30	0·1 g. anthraquinone in toluene ...	43·0	36·2	32·3	30·5	28·6	26·6	25·3	23·7	21·6
17	blank in toluene ...	29·8	27·3	25·4	22·4	20·0	17·2	15·7	14·2	13·3
72	0·1 g. anthraquinone in benzene ...	40·9	39·8	40·2*	37·2	35·2	38·4*	34·3	34·1	33·4
80	blank in benzene ...	41·2	39·7	39·2*	37·0	36·6	39·1*	34·5	32·5	33·1
90	0·076 g. benzoquinone	13·3	11·1	8·7	7·3	6·0	5·2	5·1	3·6	4·0
73	0·1 g. α-naphthaquinone	19·9	21·4	21·6	23·4	22·6	24·8*	23·5	26·0*	26·4
75	0·1 g. β-naphthaquinone	30·0	32·9	32·4	38·4*	36·5	34·7	34·5	33·3	31·7
82	0·03 g. phenanthraquinone	41·1	38·4	36·2	40·0*	38·1	36·3	38·9*	36·2	34·2
84	0·03 g. acenaphthaquinone ...	41·0	39·2	41·3*	39·0	...	39·9	35·8	32·8	...

in benzene alone is more rapid than in toluene even after adding anthraquinone. Benzoquinone is a strong inhibitor, probably owing to the absorption of the active light rays by its intensely yellow solution. The rapid diminution in the volume of oxygen absorbed is remarkable as there was no obvious colour change during the progress of the reaction. Similar effects were observed with more dilute solutions, the absorption for a solution containing 0·013 g. in 20 c.c. being 26·4 c.c. initially and 7·5 c.c. after 3 hours. The naphthaquinones were attacked, the solutions becoming paler as the reaction proceeded and this doubtless accounts for the initial retardation and subsequent increase in velocity. Phenanthraquinone and acenaphthaquinone solutions were completely bleached in about 15 minutes and hence their effect on the course of the reaction was negligible.

A series of experiments similar to the above was conducted using 10 c.c. of pure benzaldehyde, and almost identical results were obtained when allowance was made for the reduced rate of oxidation in absence of a solvent. Benzoquinone as before reduced the rate considerably, 0·017 g. giving rise to an initial oxygen absorption of 10·7 c.c. compared with 27·5 c.c. for benzaldehyde alone. The other quinones had little or no effect, the action of α-naphthaquinone being the most marked.

Before these experiments were made the rate of oxidation of different quantities of benzaldehyde in the same tube was measured and the rate found to be very nearly independent of the quantity. For example with 10, 20 and 30 c.c. of aldehyde the volumes of oxygen absorbed in 40 minutes were 53·3, 56·5 and 55·6 c.c., respectively, showing that the reaction takes place almost entirely at the surface of the tube which is always covered with a layer of liquid by splashing. If the liquid could be regarded as nearly saturated with oxygen and reaction took place throughout the mass, the larger volume would absorb most; if on the other hand the reaction rate were controlled by the speed at which the oxygen could dissolve, the small volume should absorb most, since in this case the largest surface is exposed to the gas.

The inhibiting action of phenolic compounds.

The antioxygenic action of pyrogallol and similar phenols has been extensively studied by other investigators and particularly by Moureu and Dufraisse (*loc. cit.*), but the latter authors allowed the reaction to proceed without agitation and in very feeble light so that it was not certain what relation their results would bear to those obtained under our experimental conditions. A series of experiments was therefore conducted using 10 c.c. of pure benzaldehyde in each case with small quantities of phenolic compounds. Table VIII shows

TABLE VIII.

Oxidation of benzaldehyde in presence of phenols, 30·5°.

No. 114	103	109	104	105	110	111	112	113	108
Blank	Quinol 4·3 mg.	Quinol 3·2 mg.	Quinol mono-methyl ether 4·1 mg.	Quinol dimethyl ether 4·5 mg.	Catechol 4·5 mg.	Resorcinol 4·5 mg.	Pyrogallol 4·5 mg.	Pyrogallol 3·2 mg.	Pyrogallol trimethyl ether 4·5 mg.
29·5	2·0	4·8	3·1	23·0	4·5	12·6	3·1	3·8	25·8
28·3	2·6	4·8	4·2	20·6	4·1	9·9	2·7	2·8	24·5
26·7	3·3	4·9	4·3	19·4	4·0	8·9	2·8	2·6	24·4
25·3	3·2	3·8	4·0	18·0	3·9	8·7	3·3	2·8	23·3
23·0	3·0	4·8	4·1	16·5	3·7	7·5	3·7	3·0	...
6·0[1]	2·8	5·3	4·3	16·3	4·7	7·9	3·8	3·5	23·8
...	4·0	5·3	4·6	16·9[2]	4·6	7·3	2·8	4·7	22·6
23·3	3·8	5·5	4·5	15·4	4·5	8·0	4·2	5·4	...
19·1	3·1	5·6	4·5	15·3	4·7	7·3	4·8	7·0	...
...	...	6·5	4·4	...	4·7	6·9	6·1	7·7	...
...	...	6·7	4·2	...	5·0	6·7	6·8	8·7	...
...	...	6·8	...	...	...	6·9	8·1	10·3	...
...	...	...	...	...	...	7·0	8·7	12·1	...
...	...	...	...	...	...	...	10·7	14·2	...
...	...	...	...	...	...	...	13·3	16·5	...

[1] No bubbling.

[2] Oxygen added.

the results obtained, the figures representing c.c. of oxygen absorbed in successive periods of 20 minutes under standard conditions as to light intensity and rate of bubbling.

It is evident from these figures that all the compounds tested containing a free hydroxyl group were powerful inhibitors whereas the ethers had a much smaller effect. The antioxygenic action was moreover not permanent as shown by the values for quinol in expt. 109 and for pyrogallol, the increase in rate after three hours with the latter substance being very marked. In all cases of retardation the solutions become deep yellow, but attempts to isolate the coloured compound were unsuccessful. Absorption of light by this compound would not however account for the low rates of oxidation observed, as these were lower than those measured with no illumination (*cf.* next section).

Reaction in the dark.

At intervals during the measurements of the reaction velocity under the influence of light, comparative experiments were made in which the aldehyde was kept in the dark. Table IX shows some of the results, the volume of solution being 20 c.c. in the first four experiments and 10 c.c. in the others.

TABLE IX.

Absorption of oxygen in the dark; c.c. in 20 m., 29·5°.

No. 26	28	29	51	115	116	117	114
50 per cent. toluene solution			50 per cent benzene	No solvent		3·2 mg. pyrogallol	In light
6·1	6·8	8·4	33·4[1]	19·8	18·5	1·1	29·5
4·2	4·8	6·2	9·7	17·8	19·1	0·6	28·3
3·6	3·8	4·5	5·4	19·0	19·1	...	26·7
3·3	26·5[1]	3·4	4·6	18·5	18·7	...	25·3
3·3	6·5	3·1	...	18·8	17·9	0·8[2]	23·0
3·3	3·3	2·9	...	18·4	17·5	...	...
3·1	2·3	2·8	...	...	...	...	...
2·7	2·3	2·8	...	...	...	0·8[2]	...
2·7	2·3	2·7	...	...	...	...	...

[1] Exposed to light. [2] Total for 1 hour.

A striking feature of these figures is the rapidity of the oxidation of pure benzaldehyde in the dark when compared with that of its solutions. The retardation produced by adding 50 per cent. of toluene is even greater than in the case of the corresponding quantity of benzene and is evidently due to some specific action of the former solvent, as it has already been shown that there is a similar relation in the case of the light-catalysed reaction. The acceleration produced by light is much greater with solvents, the total absorption being actually larger in spite of the smaller absorption in the dark. The figures for the toluene solutions show that the rate of absorption at the beginning of the reaction is greater than when it has proceeded for some time, and in this respect they correspond with the observations of Moureu and Dufraisse. The values in expts. 28 and 51 immediately after removing the source of illumination indicate an after-effect. In the second case measurements were taken at 10 minute intervals, and the actual values were 5·9, 3·8, 2·9 and 2·5 c.c., showing that about half an hour is required for the effect of the illumination to die down. The inhibiting action of pyrogallol is greater in the dark than in light, and a slight tendency for the rate to increase with time was observed, 1·5 c.c. of oxygen being absorbed in an hour when the experiment had been in progress for four hours. A similar effect noticed by Moureu and Dufraisse was ascribed to distillation of the benzaldehyde in the reaction tube so that it was freed from the pyrogallol, but this explanation is not applicable in the present experiments.

The temperature-coefficient of the reaction.

A few measurements of the temperature-coefficients of the reaction in the dark and in light using pure benzaldehyde were made. Sufficiently concordant results to give accurate values were difficult to obtain, but the mean figures for absorption gave the following temperature-coefficients :—

In the dark	20·5–30·5°	1·32	30·5–40·5°	1·10
In light	25·0–35·0°	1·09	30·5–40·5°	1·18

Reiff (*loc. cit.*) obtained the value 1·3 for the range 15–25° and pointed out that this is characteristic of a diffusion reaction.

Discussion of results.

The results so far obtained are insufficient to justify any generalisations regarding the nature of the reactions, but serve to indicate the direction in which further work should proceed. While not directly at variance with any theories previously advanced, they show that numerous factors must be taken into consideration and that the entire mechanism of the reaction may vary according to the conditions. In the case of benzaldehyde, solvents have a marked effect, benzene and toluene retarding the reaction in the dark, but accelerating it in light if not present in too large a proportion. The accelerating influence of benzene is greater than that of toluene, while an experiment with *p*-xylene showed that this substance inhibits the reaction almost completely. There thus appear to be two opposing factors introduced into the photochemical reaction by the addition of solvents, one increasing the velocity by a dilution effect and the other diminishing it in different degrees depending upon the oxidisability of the solvent itself. The relation between reaction velocity and concentration is obscure and requires investigation in a greater variety of solvents, while minor effects such as the small rise in reaction rate soon after the commencement of the reaction in the light, and the rapid initial fall in the dark, should not be neglected.

The greatest difficulty encountered has been the inconsistency of results obtained under apparently identical conditions. Although some improvement might be effected by a device for exposing the liquid to the action of light and oxygen in the form of a thin film moving at a constant rate, the main variations seem to depend upon minute quantities of impurity in the benzaldehyde itself, the nature of which it has not been possible to determine. The addition of various chlorine compounds has been found to have little or no effect, while anthraquinone is the only substance observed to have a definite accelerating influence; even this is only in toluene solutions. The well-known antioxygenic action of phenolic compounds has been confirmed, but it has been shown that the retarding effect in light is far less than in the dark, pyrogallol in particular soon tending to become less active, presumably owing to its gradual decomposition.

The similarity of the temperature coefficients in light and in the dark, and the independence of the rate and the volume of the liquid, indicate that the reaction in both cases takes place mainly at the surface, Reiff having clearly established this fact for the reaction in the dark. The after-effect noticed upon removing the source of light shows the presence of an intermediate compound, but this must be either a different body to the one formed in the dark or its equilibrium concentration must be greatly diminished when not exposed to light. The different behaviour of pyrogallol in light and in darkness suggests that the former view is more probable.

The oxidation of toluene differs considerably from that of benzaldehyde. It takes place very slowly or not at all in the absence of a catalyst and appears to be a volume reaction, the rate probably depending upon the extent of the water-toluene interface. Although formed in small quantities, benzaldehyde is not the intermediate product which determines the rate of the reaction, the active substance being hydrogen peroxide, an or organic peroxide which is readily decomposed, but is not destroyed by pyrogallol, this compound actually increasing the rate of reaction instead of reducing it as in the case of benzaldehyde.

In conclusion we wish to express our best thanks to Mr. S. K. Kulkarni Jatkar for much assistance during the course of the experiments.

Department of General Chemistry,
Indian Institute of Science,
Bangalore.

[Accepted, 24-3-31.]