XXXIV.—*The Photochemical Interaction of Acetaldehyde and Oxygen.*

By Edmund John Bowen and Edmund Lagesen Tietz.

In 1835 Liebig (*Annalen*, **14**, 139) observed that acetaldehyde absorbed oxygen at the ordinary temperature, giving, according to him, acetic acid. Later, several investigators, working on "autoxidation," found that benzaldehyde and some other aldehydes gave peroxides with oxygen, but there seems to be no reference in the literature to the formation of a peroxide of acetaldehyde under these conditions. Chastaing (*Ann. Chim. Phys.*, 1877, **11**, 145) found that acetic acid was formed in the photochemical reaction.

The experiments now described show that a peroxide of acetaldehyde is quantitatively formed, and that it is a moderately stable substance; moreover, it is formed thermally as well as photochemically when liquid acetaldehyde is shaken with oxygen (*Nature*, 1929, **124**, 914). There are two possible peroxides, *viz.*, peracetic acid, $CH_3{\cdot}CO{\cdot}O{\cdot}OH$, and diacetyl peroxide, $CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3$, both of which have been prepared in other ways. The latter is hydrolysed to the former by water (Clover and Richmond, *Amer. Chem. J.*, 1903, **29**, 179). Bäckström (*Medd. K. Vetenskapsakad. Nobel-Inst.*, **6**, No. 16) has recently investigated the formation of a peroxide from benzaldehyde, and shown that the thermal and photochemical changes are chain reactions.

EXPERIMENTAL.

Apparatus.—A quartz mercury lamp contained in a water-cooled box served as a light source, and the light passed through a quartz window into a thermostat which contained the reaction vessel. This was made of clear fused quartz, joined to glass where necessary by mercury-sealed ground joints.

The purest specimens of acetaldehyde obtainable from Kahlbaum and Harrington were used, and the results were the same with either specimen.

1. *The Photochemical Oxidation of Gaseous Aldehyde by Air.*—A current of air, dried with sulphuric acid and filtered through glass wool, was drawn by a water-pump through a bubbler containing acetaldehyde at 0°, then through the quartz reaction bulb, and finally through potassium iodide solution. Iodine was liberated, showing that a peroxide had been formed by exposure of the gases to ultra-violet light. Control experiments showed that air alone passing through the reaction vessel did not liberate iodine, and that the excess aldehyde caught in the potassium iodide solution did not absorb any of the iodine liberated. The peroxide formed partly condensed in the reaction vessel, but by turning off the light and continuing the gas flow for several minutes the whole of it could be carried over. The temperature of the thermostat was 20° in the first experiments; it was later raised to 30° to diminish the time for " washing out " the peroxide after the light had been turned off. Experiments were made with rates of gas flow between 1000 and 20,000 c.c./hour, and it was found that at rates above 4000 c.c./hour the amount of peroxide formed was independent of the rate of flow, and linearly proportional to the time of exposure. The peroxide must be formed by a chain reaction, for the number of g.-mols. produced in these experiments per minute was about 10^{-3}, whereas the energy in the light absorbed, calculated from an approximate knowledge of the energy distribution of the lamp and the absorption spectrum of acetaldehyde, was about 10^{-6} g.-mol. quantum per minute. The chain length under these conditions was therefore about 1000 molecules, but the exact value of this is unimportant, as will be clear from section 2.

2. *Effect of Wave-length and Intensity of the Light.*—The above experiments were made with the full light of the mercury lamp. Experiments were next performed using screens to cut down the light intensity, in conjunction with filters. The screens were metal sheets with small perforations, and their transmissions were calibrated with a thermopile and an electric lamp. The following filters were used :

	Mercury lines transmitted.
(1) Vita-glass	>2900 Å.
(2) Auramine-O in aqueous solution (1 cm. of 0·0125%)	3135—2700
(3) Chlorine–bromine filter	2900—2485

The results are in Table I, where I represents the light intensity, y the titre against $N/100$-thiosulphate of the iodine liberated, and the filters used are denoted by their respective numbers in the foregoing scheme.

Table II gives the ratio of the mean titres to the square root of the light intensity, and shows clearly that the reaction is essentially

TABLE I.

Rate of flow of gases, 7000 c.c./hour. Time of exposure, 30 minutes.

	y.				y.		
I.	(1).	(2).	(3).	I.	(1).	(2).	(3).
48·5	29·08	54·29	32·14	16·0	16·19	30·72	18·57
	29·29	54·53	33·33		15·95	31·20	17·62
	28·06	54·05	30·71		15·71	30·48	17·62
23·3	18·33	36·91	21·67	7·5	10·24	21·91	13·33
	19·76	38·58	20·95		10·48	22·39	13·33
	19·05	37·62	20·83		10·48	20·95	12·86

TABLE II.

		$y/\sqrt{I}$.		
I.	$\sqrt{I}$.	(1).	(2).	(3).
48·5	6·96	4·14	7·80	4·61
23·3	4·83	3·95	7·81	4·38
16·0	4·00	3·99	7·70	4·49
7·5	2·74	3·74	7·94	4·80

the same throughout the ultra-violet absorption band of acetaldehyde, the rate being proportional to the square root of the light intensity. This is a rather surprising result.

3. *Effect of Acetaldehyde and of Oxygen Concentration.*—The aldehyde concentration was changed by introducing a variable by-pass and a flow-meter across the acetaldehyde bubbler, and the oxygen concentration was varied by using oxygen–nitrogen mixtures from cylinders, a large bottle being interposed to ensure mixing of the gases. The composition of the mixtures was obtained from flow-meter readings.

Table III gives the variation of the rate (as measured by the iodine titre, y) with the relative aldehyde concentration, [A], and Table IV the variation with oxygen concentration in the oxygen–nitrogen mixture.

TABLE III.

Exposure, 15 mins.

Vita-glass filter.				Chlorine–bromine filter.			
[A].	y.	[A].	y.	[A].	y.	[A].	y.
6·9	0·83	7·2	0·95	7·1	0·95	7·1	1·07
14·6	1·79	14·4	2·38	14·5	2·14	14·3	2·26
28·1	3·69	28·6	5·12	29·0	4·76	28·0	4·53
42·9	5·48	42·0	7·38	42·9	7·62	44·1	7·50
56·5	7·50	56·7	9·53	58·0	10·59	56·8	10·00
71·4	9·53	57·0	9·05	71·2	12·38	71·3	12·62
85·4	11·07	71·2	11·69	85·8	15·26	85·4	14·88
85·7	11·19	71·4	11·54	100·0	17·62	100·0	17·38
100·0	13·34	100·0	13·70				

TABLE IV.

Exposure, 30 mins. Full light.

O_2, %.	y.	O_2, %.	y.
24·1	40·2	53·3	35·0
34·2	39·0	62·3	35·7
41·5	39·0	74·0	36·4
47·8	34·8	100·0	38·3

From these results it appears that the reaction rate is proportional to the aldehyde concentration and independent of the oxygen concentration.

Before the mechanism of the reaction could be explained, it was necessary to know whether the variation of the rate with aldehyde concentration was due to variations in the amount of light absorbed. This was therefore examined at different wave-lengths by means of a quartz spectrograph of a new type, designed by Mr. J. H. Jeffree, in which a quartz sodium photoelectric cell and Lindemann electrometer are used to measure the light in the spectrum formed by the instrument, which had also been used to investigate the transmissions of the filters described above. Between 3200 and 2800 Å., the absorption of gaseous acetaldehyde in the photochemical cell was about 90%, and between 2700 and 2400 Å. about 74%. The absorption was almost independent of the aldehyde concentration, showing that most of the mercury lines in the above regions were totally absorbed, the others being transmitted.

The kinetics of the reaction are $dx/dt = k\sqrt{L}[A]$, where L is the light absorbed, and [A] the aldehyde concentration. An explanation of this result can be given by the following chain mechanism :

		Rate.
1.	$A + h\nu \longrightarrow A^*$	k_1L
2.	$A^* + O_2 \longrightarrow AO_2^*$	$k_2[A^*][O_2]$
3.	$AO_2^* + A \longrightarrow A^* + AO_2$	$k_3[AO_2^*][A]$
4.	$2AO_2^* \longrightarrow ?$	$k_4[AO_2^*]^2$

Reactions 2 and 3, by repetition, produce chains, which are broken by reaction 4. For the steady reaction, we have

$$d[A^*]/dt = 0 = k_1L + k_3[AO_2^*][A] - k_2[A^*][O_2]$$

and $$d[AO_2^*]/dt = 0 = k_2[A^*][O_2] - k_3[AO_2^*][A] - k_4[AO_2^*]^2$$

whence $$k_1L = k_4[AO_2^*]^2$$

Then $$d[AO_2]/dt = k_3[AO_2^*][A] = k_3\sqrt{L}\sqrt{k_1/k_4}[A]$$

When peracetic acid reacts with potassium iodide the solution should become alkaline :

$$CH_3{\cdot}CO{\cdot}O{\cdot}OH + 2KI \longrightarrow CH_3{\cdot}CO_2K + KOH + I_2$$

Experiments showed, however, that after the iodine titration the solution was always slightly acid. This point is referred to again in section 4.

4. *Oxidation in the Liquid and the Dissolved State.*—The apparatus used for these experiments consisted of a small quartz tube to contain the liquid, mounted in a shaking machine in a thermostat, and connected by flexible tubing to a gas burette containing oxygen. As solvents, water, acetic acid, and hexane were tried, as they are transparent to the light absorbed by acetaldehyde. The peroxide was estimated by adding the liquid to potassium iodide solution as before, and was found to be formed very rapidly in liquid aldehyde and in its solutions in the above three solvents, and once formed, to be very stable, showing no decomposition in one hour, except in the aqueous solutions, in which it almost all reacted in 20 seconds. This latter fact was utilised to determine the nature of the peroxide. Liquid aldehyde was shaken with oxygen to produce some peroxide. One portion (*a*) was added at once to neutral potassium iodide solution, the liberated iodine titrated with *N*/100-thiosulphate, and the remaining acidity estimated with *N*/100-baryta solution. The other portion (*b*) was added to water, and the peroxide allowed to react with the excess aldehyde to give acetic acid. The acidity of this solution was then estimated. The following table gives some results :

	Expt. 1.		Expt. 2.	
Portion.	Iodine titre.	Acid titre.	Iodine titre.	Acid titre.
(*a*)	24·97	8·28	25·32	7·56
(*b*)	0·0	45·77	0·0	46·68

These figures can be explained by assuming that the peracetic acid first formed partly reacts with aldehyde to give acetic acid, but that the reaction is limited by the combination of the acetic acid with peracetic acid to give diacetyl peroxide, according to the equations

$$CH_3{\cdot}CO{\cdot}O{\cdot}OH + CH_3{\cdot}CHO \longrightarrow 2CH_3{\cdot}CO_2H,$$
$$CH_3{\cdot}CO{\cdot}O{\cdot}OH + CH_3{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O.$$

Diacetyl peroxide reacts with potassium iodide to give a neutral solution : $(CH_3{\cdot}CO{\cdot}O{\cdot})_2 + 2KI \longrightarrow 2CH_3{\cdot}CO_2K + I_2$, and the average iodine titre value above (25·15 c.c.) represents 12·57 c.c. of *N*/100-peroxide. The average acid titre after the iodine titration (7·92 c.c.) probably represents a little excess acetic acid. The increase in acidity on standing in aqueous solution should then be represented by 46·22 − 7·92 = 38·3 c.c. of *N*/100-acid. The reaction of the peroxide on standing in water must be $(CH_3{\cdot}CO{\cdot}O{\cdot})_2 + CH_3{\cdot}CHO \longrightarrow 3CH_3{\cdot}CO_2H$, representing an acidity of 3 × 12·57 = 37·71 c.c. of *N*/100-acid, in close agreement with the calculated figure, 38·3 c.c.

It seems necessary to assume the formation of diacetyl peroxide to account for the approximate neutrality of the solutions after titration of the iodine liberated. The results given in Table VI for hexane–aldehyde mixtures show an even greater approach to neutrality than the figures just given.

Although the peroxide was found to be quite stable when formed in pure liquid aldehyde, the reaction rates were very irregular, due to the high vapour pressure, which, by producing a buffer of vapour, prevented the oxygen from freely dissolving in the liquid. The absorption of oxygen also took place rapidly in the dark. Very reproducible results were obtained for solutions of acetaldehyde in glacial acetic acid and in hexane. The thermal reaction in these solvents was small. Table V gives some results for acetic acid solutions, the amounts of oxygen absorbed (as given by gas-burette readings), and of peroxide formed (AO_2, as deduced from the iodine titre) being recorded as g.-mols. × 10^{-4}.

TABLE V.

Ratio, by vol., $C_2H_4O : C_2H_4O_2$.	Time, mins.	$O_2 \times 10^4$.	$AO_2 \times 10^4$.
1 : 1	1	1·72	1·45
	2	3·08	2·51
	3	4·27	3·36
	4	4·87	3·89
(Dark reaction	15	0·35	0·28)
1 : 2	1	1·64	1·51
	3	4·85	4·43
	5	7·56	6·30
(Dark reaction	15	0·39	0·39)
1 : 5	1	1·20	1·44
	2	2·34	2·54
	3	3·03	3·07
	5	4·72	4·45
	7	7·38	6·50
(Dark reaction	15	0·05	0·27)
1 : 8	2·5	1·47	1·61
	5	3·34	3·22
	7	4·44	4·10
	10	6·24	5·50
	15	6·77	6·01
(Dark reaction nil.)			
1 : 10	2·5	0·89	0·99
	5	2·15	2·13
	7	2·72	2·56
	10	3·78	3·50
	15	6·30	5·33
(Dark reaction nil.)			

These results show that the amount of peroxide formed increases linearly with time, and that the rate is proportional to the aldehyde concentration when it is below 20%. The most important result, however, is the agreement between the number of molecules of oxygen absorbed and of peroxide produced. In acetic acid solutions, diacetyl peroxide formation can occur without the preliminary decomposition of some of the per-acid by reaction with aldehyde.

Table VI gives results for hexane solutions. The light intensity was varied with screens as previously described, and its relative values are denoted by I. The iodine titre y (c.c. $N/100$-thiosulphate) is a measure of the peroxide produced.

TABLE VI.

Ratio, by vol., $C_2H_4O : C_6H_{14}$.	I.	y.	$y/\sqrt{I}$.	Excess acidity after iodine titre (c.c. $N/100$).
1 : 2	48·5	69·1	9·93	4·5
	23·3	45·0	9·32	2·5
	16·0	41·6	10·4	2·0
	7·5	26·8	9·77	2·0
1 : 3	48·5	42·3	6·08	2·5
	23·3	28·7	5·94	2·0
	16·0	27·3	6·82	2·0
	7·5	21·4	7·81	2·0
1 : 5	48·5	25·6	3·68	0·3
	23·3	18·4	3·81	0·0
	16·0	14·6	3·65	0·0
	7·5	10·8	3·94	0·0

These results are in complete agreement with those of Tables I and II, and show that the rate of peroxide formation is proportional to the square root of the light intensity and to the aldehyde concentration. The amount of free acid found after the iodine titre is small, showing that diacetyl peroxide is probably formed.

5. *The Inhibition by Ethyl Alcohol.*—The introduction of an inhibitor into the system will alter the chain-breaking mechanism from the bimolecular reaction $2AO_2^* \longrightarrow ?$ to one of the type $AO_2^* + X \longrightarrow ?$ The rate of reaction will then become proportional to the light intensity instead of to its square root. That this is actually the case is shown in Table VII, which gives results for the rate when alcohol was added.

TABLE VII.

Ratio by volume. Aldehyde : hexane : alcohol = 2 : 4 : 1.

I	4·85	4·85	2·33	2·33	1·60	1·60
y	33·9	34·1	16·4	16·6	11·5	11·3
$y/\sqrt{I}$	6·99	7·03	7·04	7·19	7·19	7·07

From this result it is apparent that the effectiveness of an inhibitor at a given concentration must depend on the light intensity in this reaction. Assuming that the mechanism of inhibition is that described above, it can be shown that for fixed light intensity and aldehyde concentration the rate should vary according to the equation $y^2 + \alpha X y = \beta$, where y is the rate and X the inhibitor concentration; whereas for fixed light intensity and inhibitor concentration, the ratio of rate to aldehyde concentration should be constant. These conclusions are tested by the results given in Tables VIII and IX, for solutions in hexane. The former table gives X as the percentage of alcohol, y as the iodine titre, and the value of α as calculated from the above equation with $\beta = 5242$.

TABLE VIII.

Aldehyde concentration, 33%.

X.	y.	a.
0	72·4	—
1·33	55·5	29·3
6·67	29·1	22·6
12·5	11·3	36·3

TABLE IX.

Alcohol concentration, 14·3%.

[A].	y.	[A] − 14·3.
14·3	1·9	0
21·42	6·1	7·1
28·56	10·5	14·3
35·7	22·0	21·4

Although the variation of velocity with inhibitor concentration is approximately as expected, yet its variation with aldehyde concentration can only be made to agree with the theory if the inhibitor concentration is subtracted from the aldehyde concentrations (see Table IX). The interpretation of this is that the alcohol first combines with activated aldehyde molecules to give a compound which is the actual inhibitor, thereby reducing the effective aldehyde concentration. These experiments are being continued.

6. *Statical Measurements on Gaseous Mixtures.*—It was suggested to us by Mr. A. C. Egerton that, as peroxides are formed as intermediate compounds in the oxidation of hydrocarbons, experiments on the effect of " anti-knock " substances on this reaction would be interesting. For this purpose, gaseous mixtures of acetaldehyde and oxygen at total pressures between 60 and 20 cm. of mercury were introduced into a quartz bulb connected to a mercury manometer, and the reaction was followed by the diminution of pressure which occurs when the mixture is exposed to ultra-violet light. The pressure change–time curves for the complete reaction were found to begin with a long linear portion. When the ratio of acetaldehyde to oxygen was greater than 3 : 2, the rate after the initial period fell off gradually to an end-point, while when the ratio was less than this, the end-point was approached abruptly. Tables of results for these measurements are not given because a complete explanation depends on the nature of the final products, which were found by analysis to be complex, and to contain carbon dioxide, monoxide, and acetic acid. The initial rate of reaction was found to be approximately proportional to the square root of the light intensity and to the aldehyde pressure, and independent of the oxygen pressure, in agreement with the results derived from estimation of the peroxide.

The effect of introducing small quantities (0·1—5 mm.) of the vapour of anti-knock substances was as follows.

Iron carbonyl. A dense white mist was formed when the light was turned on. The oxidation of the aldehyde was inhibited for a long period, proportional to the amount of iron carbonyl present. At the end of the induction period the mist practically disappeared, and the reaction suddenly began at a rate almost equal to its value in the absence of the inhibitor. A red powder (Fe_2O_3 ?) was left in the reaction vessel.

Nickel carbonyl. The quantity introduced, owing to the higher vapour pressure, was about ten times that of iron carbonyl. A dense mist was formed, and a white solid deposited, and the reaction was inhibited completely.

Selenium diethyl. A dense mist was again formed, but no induction period was produced; instead, the reaction proceeded at a slow rate which gradually increased as the mist disappeared. Great difficulty was experienced in removing the last traces of selenium compounds from the reaction vessel after these experiments.

Lead tetraethyl. The vapour of this substance had no effect on the reaction rate.

Ethyl iodide. The introduction of this substance decreased the rate of reaction greatly, without producing any induction period.

These results show that anti-knock substances do not all act as inhibitors for this reaction. Lead tetraethyl does not affect the reaction at all. The results for ethyl iodide can be explained as an inner filter effect. It is uncertain whether iron and nickel carbonyls act as direct inhibitors or whether the mist formed merely scatters the light. The most that can be said is that an apparently equally heavy mist is formed with selenium diethyl, without the production of an induction period. The inhibiting effect of iron carbonyl is inversely proportional to the aldehyde pressure, which is some evidence that it acts as a direct chain breaker.

Summary.

1. A peroxide is formed when gaseous, liquid, or dissolved acetaldehyde is exposed in presence of oxygen to ultra-violet light. The reaction has been examined in different spectral regions. In the liquid and the dissolved state the peroxide is also formed in the dark.

2. The rate of reaction is proportional to the square root of the light intensity and to the aldehyde concentration, but independent of the oxygen concentration. This can be explained by a chain mechanism involving the formation of peracetic acid as the first product.

3. Reasons are given to show that diacetyl peroxide is formed by further reactions of the peracetic acid.

4. Alcohol acts as an inhibitor when added to hexane solutions of aldehyde. As expected, the rate becomes directly proportional to the light intensity, instead of to its square root.

5. Anti-knock substances do not all act as inhibitors of the photochemical reaction between acetaldehyde and oxygen.

We are indebted to Mr. Egerton for the anti-knock substances, and to the Royal Society for a grant to purchase the quartz spectrograph used in this work.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL AND TRINITY COLLEGES,
OXFORD.

[*Received, December* 30*th*, 1929.]