

229. *The Photochemical Oxidation of Formaldehyde and Acetaldehyde.*

J. E. CARRUTHERS and R. G. W. NORRISH.

DURING the course of the experiments upon the photochemical oxidation of formaldehyde and acetaldehyde, now described, estimations were made of the quantum efficiencies of the processes, showing that the oxidation proceeds in both cases by a chain process involving a short chain

Patat (*Z. physikal. Chem.*, 1934, *B*, **25**, 208; see *ibid.*, *B*, **27**, 431), investigating the primary process of the photodecomposition of formaldehyde, added various amounts of

oxygen in an attempt to prove the existence of hydrogen atoms in the process. He discovered that the ratio of the amounts of carbon monoxide and hydrogen liberated in the region of continuous absorption which lies beyond the region of predissociation was displaced from the normal value of approximately unity to as much as 1.47 : 1. The loss of hydrogen was explained as being due to reaction between hydrogen atoms and oxygen to give water. Although not disputing the possibility of production of hydrogen atoms in the decomposition, we think that the divergence in the value of the CO/H₂ ratio must be attributed to the oxidation process described in the following pages and is not conclusive evidence of the existence of hydrogen atoms. When oxygen is added, we are dealing with an entirely different system. Illumination results in the formation of formic acid, and although this may not be the primary product, subsequent decomposition results in the production of a larger proportion of carbon monoxide than hydrogen, as will be shown later.

In the thermal oxidation of gaseous acetaldehyde, the primary formation of peroxides (e.g., peracetic acid) has been described by Kiss and Demény (*Rec. trav. chim.*, 1924, **43**, 221), Bodenstein (*Sitzungsber. preuss. Akad. Wiss. Berlin*, 1931, III, 18), and Hatcher, Steacie, and Howland (*Canadian J. Res.*, 1931, **5**, 648). An estimation of the quantum efficiency of the photochemical reaction between acetaldehyde vapour and oxygen has been made by Bowen and Tietz (J., 1930, 234), who bubbled dry air through liquid acetaldehyde, then through a quartz reaction bulb, and finally through potassium iodide solution. When the reaction vessel was illuminated with unfiltered light from the mercury arc, iodine was liberated in the solution and was ascribed to the formation of a peroxide of acetaldehyde. The quantum efficiency, calculated from the amount of iodine liberated and from a knowledge of the approximate energy distribution of the mercury lamp, was assessed at about 1000 molecules per quantum absorbed. No direct measure of the light absorption, however, was made in their case.

It is possible, as Mr. Bowen has suggested to us, that an explanation of the difference of chain length may arise from the fact that the rate of reaction varies with the square root of the light intensity (see Bowen and Tietz, *loc. cit.*). It seems, however, doubtful, for on this basis a ratio of 1 : 50 in chain lengths would require a ratio of 2500 : 1 in light intensities, and in view of the fact that our absolute velocities were of the same order as those of Bowen and Tietz this can hardly have been possible. Bowen and Tietz did not claim to make any direct measurement of light intensity or absorption, and it is possible that the discrepancy is referable to some error in assessing the output and energy distribution of their mercury lamp.

EXPERIMENTAL.

The Oxidation of Formaldehyde and Acetaldehyde in Closed Systems.—Formaldehyde. The photochemical oxidation of formaldehyde was studied at 100° in mixtures CH₂O + O₂ and 2CH₂O + O₂; the partial pressure of formaldehyde in all cases was 100 mm.

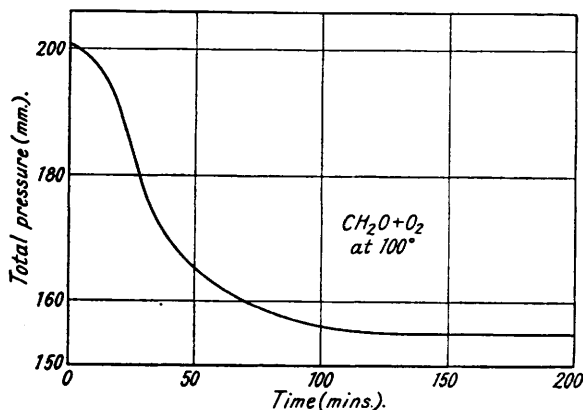
The experimental arrangements were very similar to those adopted by Norrish and Kirkbride (J., 1932, 1518) in their investigations on the quantum efficiency of the decomposition of gaseous formaldehyde. The reaction vessel was cylindrical, being double-walled and constructed of clear quartz. Distilled water was placed in the outer jacket and kept boiling by electrical heating with 32-gauge nichrome wire wound round the vessel. The connecting tubing of the apparatus was electrically heated to 90° to prevent polymerisation of formaldehyde on the walls. Pressure changes during the experiments were observed on a mercury manometer, and this was also heated. A suitable stopcock lubricant was found to be Apiezon grease "N," provided the tap did not become too hot, but in some later experiments a special rubber grease was prepared by dissolving pure shredded rubber in "Everett's" grease.

Monomeric formaldehyde was prepared by the method of Trautz and Ufer as improved by Spence (J., 1933, 1193), *viz.*, by heating paraformaldehyde, which had been thoroughly dried over sulphuric acid in a vacuum desiccator, to 110°. After rejection of the first portions of gas, which contained a large amount of water and caused formation of trioxymethylene in the trap, the remainder was condensed in liquid air. Careful redistillation effected a separation from polymerides.

Oxygen was prepared by electrolysis between nickel electrodes a 10% solution of sodium

hydroxide saturated with barium hydroxide to remove carbonates. The source of illumination in the experiments was a horizontal mercury-vapour lamp, unfiltered, mounted alongside the reaction vessel, operated at a burner voltage of 73 volts and taking a current of 3.9 amps.

Formaldehyde gas at a pressure of 100 mm., when introduced into the reaction vessel, showed very slight polymerisation—to the extent of a few mm. per hour—owing to the fact that the ground joint could not be directly heated. When a mixture $\text{CH}_2\text{O} + \text{O}_2$ at a total pressure of 200 mm. was illuminated, a rapid decrease of pressure took place, and the reaction was complete in about 120 minutes. The form of the pressure-time curve is seen in Fig. 1, from which it is clear that the reaction did not achieve a maximum speed for some minutes. The total decrease

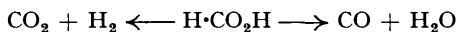


of pressure was about 46 mm. This decrease was satisfactorily accounted for on analysis of the reaction products.

The gaseous products were pumped off at -78° by means of a Toepler pump and analysed in a Bone and Wheeler gas-analysis apparatus. Carbon dioxide, oxygen, carbon monoxide, and hydrogen were recognised. Formic acid which was also a product was condensed in the freezing mixture. No peroxide was detected by the titan acid, ether-dichromate, or potassium iodide test. Estimation of the proportions of the various possible reactions led to the following data. Of the original formaldehyde after illumination

for 116 minutes there appeared 45% as formic acid, 20% as $\text{H}_2\text{O} + \text{CO}$, and 3% as $\text{CO}_2 + \text{H}_2$. Also, associated with this oxidation, about 32% of the formaldehyde polymerised, and there was a slight photochemical decomposition of the formaldehyde itself.

These data are explained by the primary oxidation of gaseous formaldehyde to formic acid according to the equation $\text{H}\cdot\text{CHO} + \frac{1}{2}\text{O}_2 = \text{H}\cdot\text{CO}_2\text{H}$. The presence of carbon dioxide, carbon monoxide, and hydrogen in the products is explained by the subsequent decomposition of the formic acid in two ways:



(see, e.g., Ramsperger and Porter, *J. Amer. Chem. Soc.*, 1926, 48, 1270; Gorin and Taylor, *ibid.*, 1934, 56, 2042; Bates and Taylor, *ibid.*, 1927, 49, 2438; Herr and Noyes, *ibid.*, 1928, 50, 2345).

The associated polymerisation has been separately studied by us (*Trans. Faraday Soc.*, 1935, 31, 195) and shown to be independent of irradiation and to be induced by the formic acid produced in the oxidation. This polymerisation, therefore, also took place in the dark after extinction of the mercury lamp. Analysis showed that no further oxidation of the formaldehyde took place in the dark.

Increasing the oxygen concentration above the equimolecular amount had little effect on the course of the reaction. The pressure fell to the same extent as before (about 46 mm.), and with the mixture $\text{CH}_2\text{O} + 2\text{O}_2$ the half-time period was 18 mins. compared with about 25 mins. for $\text{CH}_2\text{O} + \text{O}_2$. When nitrogen was added to the equimolecular mixture, however, the reduction in pressure was diminished, and the half-time period remained unaltered; e.g., in the mixture 100 mm. $\text{CH}_2\text{O} + 100$ mm. $\text{O}_2 + 400$ mm. N_2 , the pressure fell by 31 mm. during the course of the complete reaction, and the time of half-reaction was 24 mins. Probably the nitrogen exerts an inhibiting effect on the heterogeneous polymerisation reaction by preventing the diffusion of formaldehyde molecules to the walls.

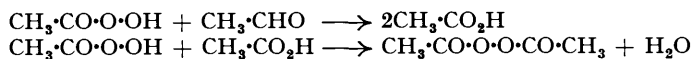
A trace of iodine vapour (about 0.2 mm.) reduced the proportion of the total reaction proceeding as polymerisation: comparative experiments showed that in the pure mixture 68% formaldehyde was oxidised, but that in the presence of the above trace of iodine as much as 97% was oxidised.

Acetaldehyde. The photochemical oxidation of acetaldehyde was studied at 30° . The reaction system consisted of a cylindrical quartz reaction vessel with optically plane ends (capacity 63 c.c.). This was kept in a water thermostat at 30° , and was connected by a ground joint to a capillary manometer. Readings of the manometer enabled the change of the total

pressure in the system to be followed. Acetaldehyde was prepared according to the directions of Leighton and Blacet (*J. Amer. Chem. Soc.*, 1933, 55, 1766) from redistilled paraldehyde. The mercury lamp used had a special type of horizontal burner, which, when mounted axially with the reaction vessel, provided with a quartz lens system a narrow converging beam of light.

On illumination of an equimolecular mixture of acetaldehyde and oxygen at a total initial pressure of 401.0 mm. with unfiltered light from the mercury arc, the pressure fell fairly rapidly, and after 200 mins. reached a steady value of 212.9 mm. The gaseous products contained oxygen (59.2%) and carbon monoxide (24.8%), together with small amounts of ethylene (1.5%) and methane (4.4%) and a trace of hydrogen. These experiments thus showed that some oxygen was unused when the total pressure of the system came to a stationary value (taken as the end of the reaction). In addition, considerable amounts of iodine were liberated from a solution of potassium iodide by washings of the condensed products. This was ascribed to the peroxide shown by many workers to be produced in the oxidation of acetaldehyde. The ratio of the initial amount of acetaldehyde present to the amount of oxygen used up when the oxidation was carried to completion was about 2 : 1.4.

Bowen and Tietz have examined the nature of the peroxide and have shown that peracetic acid first formed is converted into diacetyl peroxide by the following reactions :



These reactions are demonstrated by the reaction of the products with potassium iodide solution. Peracetic acid should give an alkaline solution, whereas diacetyl peroxide should give a neutral solution; in practice, the solution is slightly acid, so diacetyl peroxide is the chief peroxidic product—the slight acidity being explained by a small excess of acetic acid. There is also close agreement between the number of oxygen molecules absorbed and the number of peroxide molecules produced. The fact that the oxygen uptake amounted to about 1.4 mols. for 2 mols. of acetaldehyde in our static experiments confirms Bowen and Tietz's view that diacetyl peroxide is an important product.

Quantum Efficiencies of the Two Processes.—After investigation of the nature of the oxidation of formaldehyde in the light, a determination of the quantum efficiency of the process for the mean wave-length absorbed was made by comparing its rates of oxidation and of decomposition when the two reactions were carried out under identical conditions. Values for the quantum efficiency of the decomposition of formaldehyde into carbon monoxide and hydrogen are given by Norrish and Kirkbride (*loc. cit.*), the mean value within the limits of experimental error being unity. From the ratio of the rates of the two reactions, therefore, the quantum efficiency of the oxidation could be calculated directly from this figure.

The method adopted was to take the amount of oxygen used as a measure of the oxidation, and the amount of carbon monoxide produced in the illumination of pure formaldehyde as a measure of the direct decomposition. In both cases the reaction was allowed to proceed only for a short portion of the total reaction period in order that the rate of light absorption would be sensibly constant for this time.

The determinations of the quantum efficiency of the oxidation of acetaldehyde were made in approximately monochromatic light. An equimolecular mixture of acetaldehyde and oxygen was used, in which the partial pressures of the two constituents were each 200 mm. The mixture was illuminated by means of a mercury arc, between which and the reaction vessel were interposed the following filters : (1) Nickel chloride solution (7 g. $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ + 3 c.c. conc. HCl in 500 c.c. water); (2) water; (3) chlorine gas at atmospheric pressure. (This filtering arrangement is transparent to wave-lengths from 2750 to 2480 Å., the chief lines transmitted being 2654 and 2537 Å.; Bowen, J., 1932, 2236.) Care was taken when striking the arc to return the lamp to exactly the same position before every experiment, so that conditions were strictly comparable throughout the series.

A mixture of $\text{CH}_3\cdot\text{CHO} + \text{O}_2$ at 30° was illuminated for 60 mins., and the number of molecules of acetaldehyde oxidised per minute calculated from the amount of oxygen used. Oxygen was absorbed for analysis in a freshly prepared solution of sodium hyposulphite. As a comparison for the oxidation, pure acetaldehyde was illuminated, and the number of molecules decomposed per minute calculated from the amounts of carbon monoxide and methane in the products.

These two series of experiments were performed with the same pressure of acetaldehyde (200 mm.). Direct comparison of the number of molecules of acetaldehyde oxidised and decomposed per minute—as in the case of formaldehyde—gave a measure of the "chain length," *i.e.*, the number of molecules oxidised for one primary "stimulation." Further, reference to values

for the quantum efficiency of the decomposition of acetaldehyde at 30° gave, in combination with the chain length as determined above, a measure of the absolute quantum efficiency of the oxidation. The comprehensive determinations of Leighton and Blacet (*loc. cit.*) made this calculation possible. Using a monochromator, these authors determined the quantum efficiency at 30° for various pressures of acetaldehyde at wave-lengths from 2537 to 3342 Å. At 2537 and 2654 Å. the values for a pressure of 198 mm. were 0.870 and 0.793 molecule per quantum absorbed, respectively.

In Tables I and II are arranged data showing the results of these experiments on formaldehyde and acetaldehyde.

TABLE I.

(Press. of CH₂O in all cases = 100 mm.; temp. = 100°. Volumes are reduced to N.T.P.)

Oxidation of formaldehyde.

	Expt.	O ₂ used in 8 mins. illumination, c.c.	CH ₂ O oxidised, c.c.	Rate, c.c./min.
Mixture CH ₂ O + O ₂	I	3.80	7.60	0.95
Mixture 2CH ₂ O + O ₂	{ II III	2.38 2.25	4.76 4.50	4.63 0.58

Decomposition of formaldehyde.

Expt. IV. Vol. of CH₂O decomp. in 30 mins. = 1.84 c.c.

Products { CO, 1.84 c.c. }
 { H₂, 1.75 c.c. } = 0.061 c.c./min.

Expt. V. Vol. of CH₂O decomp. in 20 mins. = 1.37 c.c.

Products { CO, 1.37 c.c. }
 { H₂, 1.21 c.c. } = 0.068 c.c./min.

TABLE II.

Oxidation of acetaldehyde.

(Total press. = 400 mm.; temp. = 30°. All volumes reduced to N.T.P.)

	Expt. VI.	Expt. VII.	
Time of illumtn., mins.	60	60	
Initial vol. of CH ₃ CHO, c.c.	17.0	16.9	
Initial vol. of O ₂ , c.c.	16.60	16.45	
Final vol. of O ₂ , c.c.	15.35	15.10	
O ₂ used, c.c.	1.25	1.35	(Mean 1.30 c.c. = 0.0217 c.c./min.)

Decomposition of acetaldehyde.

(Press. = 200 mm.; temp. = 30°.)

	Expt. VIII.	Expt. IX.	
Time of illumtn., mins.	402	168	
Vol. of products (CH ₄ + CO), c.c.	1.73	0.74	
Vol. of CO, c.c.	0.86	0.37	
Vol. of CO per min.	0.00215	0.00220	(Mean 0.00217)

Formaldehyde. For the mixture 2CH₂O + O₂, the data of Table I give values for the chain length of the oxidation of 9.4 (IV) and 8.5 (V). Taking Norrish and Kirkbride's figure of 1.0 for the quantum efficiency of the decomposition of formaldehyde, we have therefore a mean value of about 9.0 molecules per quantum absorbed for the quantum efficiency of the oxidation at 100°. The corresponding value for the mixture CH₂O + O₂ is 12.6.

Acetaldehyde. From the mean of the values VI and VII for the oxidation of acetaldehyde it is seen that in 60 mins. 1.30 c.c. of oxygen are used. This represents the oxidation of about 1.85 c.c. of acetaldehyde—a rate of 0.0308 c.c./min. The decomposition experiments show that the rate of disappearance of acetaldehyde is 0.00217 c.c./min. Thus the "chain length" of the oxidation of acetaldehyde is 14.2. The quantum efficiency for the decomposition at 2654 Å. is 0.793, and so we have for the quantum efficiency of the oxidation a value of 11.3 molecules per quantum absorbed.

Experiments using a Flowing Method for the Determination of the Chain Length of the Acetaldehyde Oxidation.—Here again a measure of the light absorbed was obtained by illuminating pure acetaldehyde, determining the amount of decomposition, and then referring to Leighton

and Blacet's value for the quantum efficiency of the decomposition. Although by using a flow technique the actual molecules of reactant in the illuminated zone were continuously changing, it was arranged that at any instant the partial pressures of acetaldehyde and oxygen were each 200 mm. as in the previous experiments. This was done by passing a stream of nitrogen and oxygen in the ratio 360 : 200 through a bubbler of liquid acetaldehyde surrounded by a mixture of ice and sodium chloride at -10° (v. p. of acetaldehyde at $-10^{\circ} = 200$ mm.). The composition of the mixture passing into the reaction vessel was therefore : $\text{CH}_3\cdot\text{CHO}$, 200 mm.; O_2 , 200 mm.; N_2 , 360 mm.

The mixture of nitrogen and oxygen was stored in a large aspirator, and an automatic leveling device enabled the gas to be passed through the reaction vessel at a constant speed throughout. The speeds recommended by Bowen and Tietz (*loc. cit.*) were used, *viz.*, 7—10 l./hour.

The reaction vessel was constructed of clear quartz, and was identical in dimensions with that used in the study of the oxidation in a closed system. Experiments as before were conducted with the reaction vessel in a thermostat at 30° , and a chlorine-nickel chloride filter being used in conjunction with the mercury lamp. The gases after leaving the reaction vessel passed into an aqueous solution of potassium iodide protected by a plug of cotton wool from atmospheric ozone resulting from the operation of the mercury lamp.

In the first experiments (when the nitrogen-oxygen mixture was dried by passing through concentrated sulphuric acid) the acetaldehyde in the bubbler frequently polymerised to a colourless solid. The only cause to which this could be attributed was the carrying over of sulphuric acid spray into the acetaldehyde (even though glass wool was inserted between the drying bottles and the bubbler). Subsequently, the sulphuric acid drying arrangement was replaced by calcium chloride drying tubes. Further anomalous results were also observed; for whereas in some cases a strong iodine colour was developed in a few minutes, upon continuing to pass the mixture the colour entirely disappeared. The method adopted therefore was to add a measured excess of standard sodium thiosulphate solution to the potassium iodide at the beginning of the experiment and by back-titrating the unused thiosulphate at the end to estimate the amount of iodine liberated. This procedure gave much more reproducible results.

Since 1 g.-mol. of diacetyl peroxide liberates 2 g.-atoms of iodine, the amount of acetaldehyde oxidised to diacetyl peroxide could be calculated. Table III shows the amount of oxidation in two experiments at 30° , the composition of the gas mixture being as above.

TABLE III.

	Expt. I.	Expt. II.
Wave-length	2500—2700 Å.	
Time of illumtn., mins.	60	30
Rate of gas flow, l./hr.	7.4	9.6
Vol. of 0.00170N-Na ₂ S ₂ O ₃ used, c.c.	111	41
CH ₃ ·CHO oxidised, g.-mols. $\times 10^{-6}$	187	69.7
Vol. of CH ₃ ·CHO oxidised, c.c. at N.T.P.	4.15	1.54

From the static experiments described previously, where we also had a pressure of 200 mm. acetaldehyde, and where the intensity of illumination was the same as in these flowing experiments, it was found that 0.00217 c.c. (N.T.P.) of acetaldehyde decomposed per minute. Using this value in comparison with the data of Expt. I above, we have

$$\text{Rate of oxidation/rate of decomposition} = 31.9 : 1.$$

For Expt. II the ratio was 23.7 : 1. Taking Leighton and Blacet's figures for the quantum yield of decomposition given above, we find that these figures give a mean value for the quantum efficiency of 22.0 molecules oxidised to diacetyl peroxide per quantum absorbed.

When acetaldehyde is oxidised photochemically under these flowing conditions, therefore, it is seen again that the quantum efficiency is of the order of 20. Until more evidence is obtained, however, it is not proposed to discuss the nature of the chain, either for acetaldehyde or for formaldehyde.

SUMMARY.

(1) The photochemical oxidation of gaseous formaldehyde and acetaldehyde has been studied, and both reactions have been shown to proceed by chains of short length.

(2) The oxidation of formaldehyde takes place by way of formic acid. No peroxide or peracid was found.

(3) Quantum efficiencies for the mixtures $\text{CH}_2\text{O} + \text{O}_2$ and $2\text{CH}_2\text{O} + \text{O}_2$ have been determined.

(4) For an equimolecular mixture of acetaldehyde and oxygen the oxygen uptake corresponded to 0.7 times the volume of acetaldehyde, in agreement with the conclusions of Bowen and Tietz that diacetyl peroxide is formed.

(5) The quantum efficiency has been calculated for 30° both in a closed system and also (in the presence of nitrogen) by using a flowing method.

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DEPARTMENT OF PHYSICAL CHEMISTRY, CAMBRIDGE.

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