351. *The Oxidation of Aldehydes. Part II. The Products of their Combustion.*

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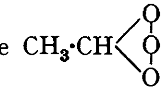
The oxidation products of a series of saturated and unsaturated aldehydes have been studied over a wide range of conditions from slow combustion to normal ignition. During the oxidation of propaldehyde and acetaldehyde the initial product consists of a relatively stable peroxide [peroxide (1)], isomeric with the corresponding per-acid. This substance, which is found at all stages prior to cool-flame inflammation or normal ignition, decomposes to give a second peroxide [peroxide (2)] and an alcohol; in aqueous solution it changes into a per-acid. The incidence of cool flames and normal ignition are shown to be conditioned by its presence in critical concentrations.

There is no evidence that per-acids or acids are formed in an excess aldehyde–oxygen medium during reaction, except at low temperatures.

At high temperatures some step-wise oxidation of aldehydes takes place to give lower members of the series.

The products from the slow combustion of the higher paraffin hydrocarbons in the gaseous phase suggest that the aldehydes formed in the early stages are able to undergo oxidation in two ways, yielding, on the one hand, a series of lower aldehydes (Pope, Dykstra, and Edgar, *J. Amer. Chem. Soc.*, 1929, **51**, 1875, 2203), and on the other, the corresponding per-acid (Bodenstein, *Sitzungsber. preuss. Akad. Wiss.*, 1931, III, 73). The evidence for the former reaction is by no means conclusive and rests mainly upon the proportions in which the reactants combine in the initial stages of the oxidation, and upon the identification of formaldehyde in the products. The difficulty of obtaining direct proof is due to there being no known easily separable derivatives of the higher aldehydes and no distinctive chemical tests for them.

Bodenstein concluded that peracetic acid was the principal intermediate formed during the oxidation of gaseous acetaldehyde, and as a result of a kinetic study of the reaction, propounded a chain mechanism in which the initial product formed from an activated aldehyde molecule and oxygen is assumed to be a peroxide of structure  $\mathrm{CH_3{\cdot}CH}\Big\langle\begin{array}{c}\mathrm{O}\\|\\\mathrm{O}\\|\\\mathrm{O}\end{array}$. This substance, by loss of energy in a collision with the walls of the containing vessel or with one of the reactant molecules, is transformed into peracetic acid.

Hatcher, Steacie, and Howland (*Canadian J. Res.*, 1932, **7**, 1491) suggest that during the induction period the following two surface reactions occur simultaneously:

$$CH_3{\cdot}CHO + 2{\cdot}5O_2 = 2CO_2 + 2H_2O$$
$$CH_3{\cdot}CHO + 1{\cdot}5O_2 = 2H{\cdot}CO_2H$$

succeeded, at a later stage, by a homogeneous reaction in which two peroxides, having the empirical formulæ $CH_3{\cdot}CHO,O_2$ and $(CH_3{\cdot}CHO)_2,O_3$, are formed.

Both these investigations and also that of Pease (*J. Amer. Chem. Soc.*, 1933, **55**, 2753) relate to reactions at and below 125° in the lower slow-combustion zone and no corresponding work appears to have been done in the cool-flame and the upper slow-combustion zone. The results are now recorded of a detailed analysis of the products formed during the oxidation of propaldehyde, acetaldehyde, acraldehyde, and glyoxal in all three zones.

Experimental.

The Aldehydes formed by the Slow Oxidation of Propane.—As a preliminary to the work an attempt was made to identify, by chemical tests, the aldehydes formed during the slow oxidation of propane. No difficulty was experienced in distinguishing between higher aldehydes and formaldehyde (Newitt and Thornes, J., 1937, 1656), but all attempts to prepare pure derivatives of propaldehyde and/or acetaldehyde failed, partly owing to the small quantities of product available and partly owing to their complexity.

Resort was, therefore, had to the spectroscope. Propaldehyde, acetaldehyde, and formaldehyde all give characteristic absorption spectra in the near ultra-violet, which are easily identifiable. The method employed was essentially that of Egerton and Pidgeon (*Proc. Roy. Soc.*, 1933, *A*, **142**, 26), who examined the absorption spectra of the products from the slow combustion of butane and pentane in a flow system at atmospheric pressure. We have, however, replaced the long absorption tube used in their experiments by a shorter steel tube fitted with thick quartz windows, and have worked at high pressures in a static system.

By employing a 20% propane–air mixture at 290—330° and 10—27 atm. pressure the spectra reproduced in Plate I were obtained. Spectrum *A* was taken as the gas mixture was being admitted to the heated reaction tube and shows four diffuse bands at 3245, 3090, 2665, and 2565 A. These correspond with the known bands of propaldehyde (Eastwood and Snow, *Proc. Roy. Soc.*, 1935, *A*, **149**, 434). In addition, two faint and very diffuse bands were observed at 2440 and 2350 A., which may possibly be a continuation of the propaldehyde series. Spectra *B*—*P* were taken at 10-minute intervals. They show the well-known formaldehyde bands increasing in intensity as the reaction proceeds, together with an internal " cut-off " extending from 3000 to 2620 A., and an external cut-off in the far ultra-violet from 2490 A. The internal cut-off occurs over the range in which the bands due to acetaldehyde are normally found, and appears to be characteristic of acetaldehyde under our experimental conditions. The external cut-off is due to olefins and organic acids, one or both of which are known to be present in the reacting medium. The external cut-off is evident at the beginning of the reaction (Spectrum *A*), decreases in intensity over the first 40 minutes, and then increases until eventually it merges with the internal cut-off (Spectra *K*—*P*).

These results show that propaldehyde is the only aldehyde present in the early stages of the oxidation and that the lower aldehydes are formed later, the concentration of formaldehyde increasing with time.

The Composition of the Reacting Medium during the Oxidation of Acetaldehyde and Propaldehyde.—In order to ascertain the conditions under which higher aldehydes undergo oxidation in two ways, an arbitrary isobar was selected on the appropriate combustion diagram, and the composition of the reacting medium at various points along it, in the lower and upper slow-combustion, and in the cool-flame zones, was determined by chemical analysis. At each point a series of experiments was carried out in which the reaction was arrested at a number of predetermined intervals before completion, and the proportions of reactants and products estimated.

The apparatus employed was that described and illustrated in Part I.

Analytical Methods.—To obtain representative samples of the gaseous and liquid products at any stage of the oxidation, two separate experiments were usually required. In the one, the reaction was arrested by removing the silica bulb from the furnace and plunging it into an ice-water bath, and a gas sample withdrawn and stored over mercury; in the other, the reaction was arrested as before and the bulb and its contents were then further cooled in liquid air, the condensed products dissolved in a measured quantity of distilled water, and aliquot parts of the solution taken for the various analyses. This procedure was rendered necessary owing to the high vapour pressure of the aldehydes.

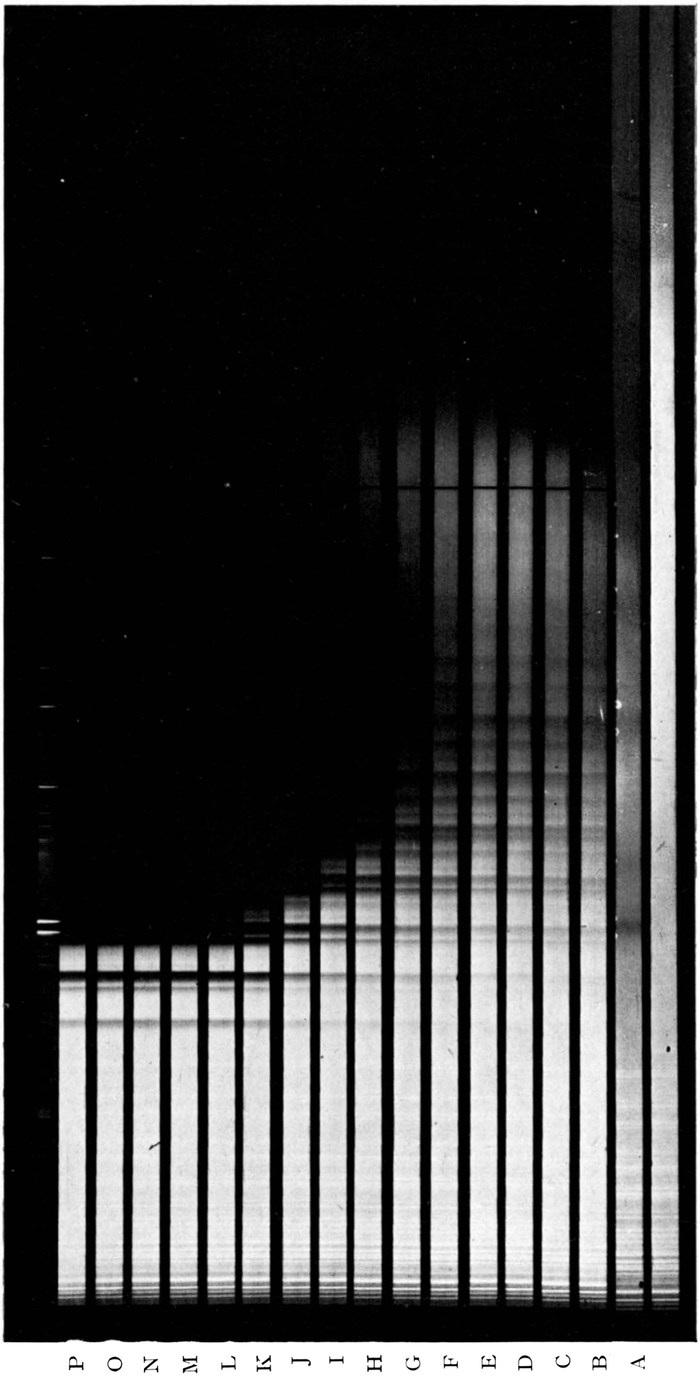
The gaseous products, after removal of aldehyde vapour by means of solid zinc chloride, were analysed by absorption with the appropriate reagents and by explosion with an excess of oxygen in a constant-volume apparatus. Analyses of the liquid products were carried out as soon as possible after the termination of an experiment, as their composition in aqueous solution was found to change on standing. With practice all the essential operations could be completed within 15 minutes.

The products from the slow oxidation of acetaldehyde include peroxides and peracetic acid, methyl alcohol, formaldehyde, traces of acetic and formic acids, the two oxides of carbon, and steam. Methane is sometimes found in circumstances in which some thermal decomposition would be expected to occur, but ethylene and acetyl peroxide do not appear to be formed. Propaldehyde gives, in addition to products corresponding with the above, ethyl alcohol, acetaldehyde, and propionic acid; no ethane or propylene survives in the products.

The methods of estimating the alcohols, total acids, total higher aldehydes, and formaldehyde have been described by Newitt and Thornes (*loc. cit.*). Peroxides and per-acids were estimated according to the method of Clover and Houghton (*Amer. Chem. J.*, 1904, **32**, 43). Their procedure distinguishes between two types of peroxide, *viz.*, those which liberate iodine immediately from a neutral solution of potassium iodide and those which liberate it slowly from an acid solution; the former we have designated peroxide (1) and the latter peroxide (2). It will be shown later that the peroxide (1), formed during the slow oxidation of aldehydes, contains a

PLATE I.

Absorption Spectra of a Reacting Propane–Oxygen–Nitrogen Mixture.

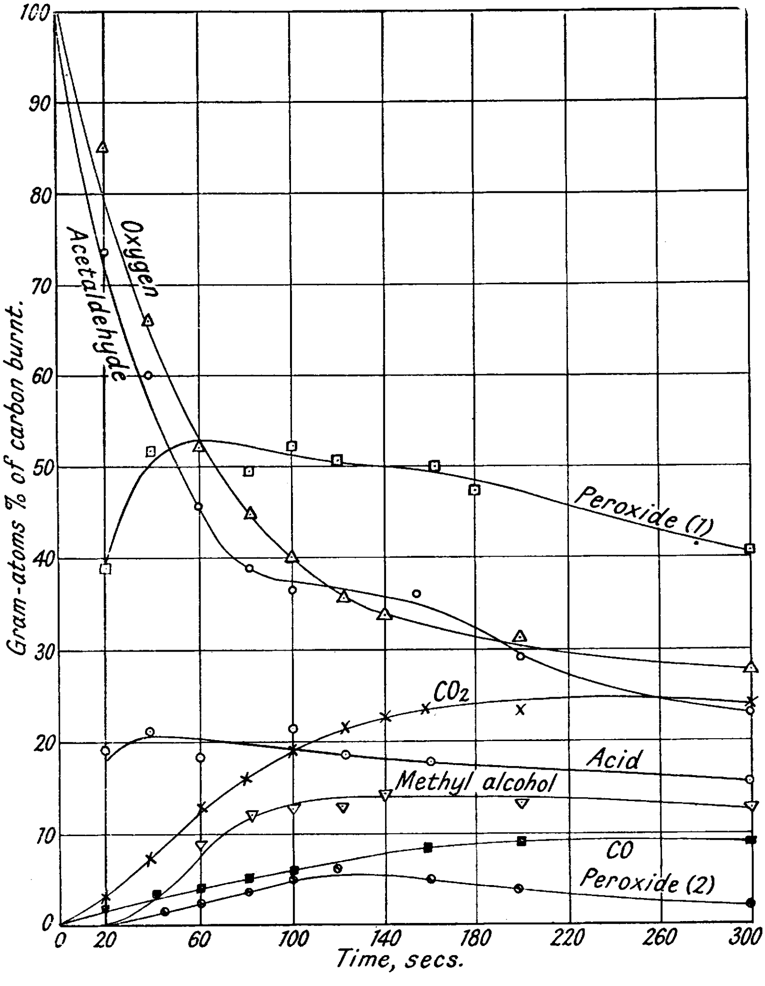


[*To face p.* 1712.

per-acid and some other non-acidic peroxide, isomeric with and changing into the per-acid on standing in aqueous solution. Peroxide (2) is probably a dialkyl or alkyl hydrogen peroxide formed by the decomposition of peroxide (1) : $C_nH_{2n+1}\cdot CHO,O_2 = C_nH_{2n+1}O\cdot OH + CO$. It may also include hydrogen peroxide and any other peroxidic substance formed by the interaction of an alkyl peroxide with an aldehyde (cf. Lenher, *J. Amer. Chem. Soc.*, **1931**, **53**, **2420**, **3737**).

Acetaldehyde. The products from an 18·8% acetaldehyde in $(2N_2 + O_2)$ mixture were examined along the 16·5 cm. isobar (Part I, Fig. 4), at 230° (lower slow-combustion zone), 237° (low-pressure ignition peninsula), 245° (single cool-flame zone), 300° (double cool-flame zone) and 350° (upper slow-combustion zone). The results, expressed as moles of each product, at various stages of the respective reactions, are summarised in Tables I—X and are shown, in several instances, by a group of curves in Figs. 1 and 2. The graphical results are expressed as g.-atoms % of carbon burnt.

FIG. 1.



Combustion products of a $CH_3\cdot CHO$ = 18·8%, $(2N_2 + O_2)$ = 81·2% *mixture in the lower slow-combustion zone ;* T = 230° *;* P = 16·6 *cm.* Hg.

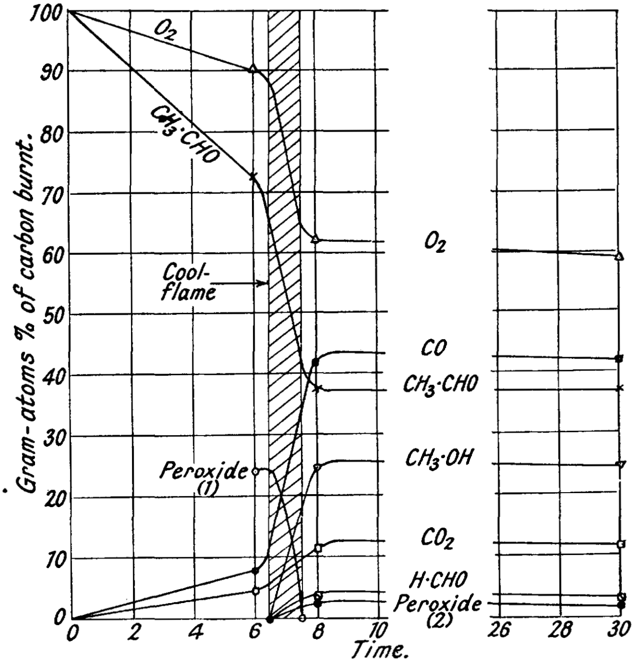
(a) *The lower slow-combustion zone* (Table I and Fig. 1). The slow combustion at 230° is accompanied, at first, by a fall in pressure, succeeded by a slow rise. The analytical data show that during the early stages of the reaction most of the aldehyde is oxidised to peroxide (1) and acid, both reaching a maximum after about 1 min., at which time nearly one-half of the reactants have been consumed. At this point peroxide (1) appears to decompose more rapidly than it is formed, giving peroxide (2) and methyl alcohol :

$$CH_3{\cdot}CHO,O_2 \longrightarrow CH_3{\cdot}OOH + CO \longrightarrow CH_3{\cdot}OH + CO_2$$

Since no formaldehyde is found at any stage of the reaction it is improbable that any oxidation of the type postulated by Pope, Dykstra, and Edgar (*loc. cit.*) is taking place.

The ratio of aldehyde to oxygen used is 1·32 after 20 secs., falling abruptly to about 0·7 in the later stages of the reaction ; the latter result is in harmony with the observation of Hatcher, Steacie, and Howland (*loc. cit.*), who found 0·62. It is also noteworthy that the ratio CO/CO_2 falls rapidly from 1 to about 0·3 as reaction proceeds, there being indications of a minimum at 1½ minutes.

FIG. 2.



Combustion products of acetaldehyde in the cool-flame zone.

TABLE I.*

Products from the combustion of an 18·8% $CH_3{\cdot}CHO$–81·2% $(2N_2 + O_2)$ *mixture in the lower slow-combustion zone.* $T = 230°$. $P = 16{\cdot}6$ cm. Hg.

Time (secs.).	0.	20.	40.	60.	80.	100.	120.	160.	200.	300.
$CH_3{\cdot}CHO$	5·55	4·09	3·39	2·57	2·10	1·98	2·00	2·00	1·60	1·41
O_2	8·00	6·90	5·43	4·14	3·41	3·16	2·85	2·62	2·57	2·28
Acids	—	0·28	0·45	0·50	0·56	0·78	0·63	0·61	0·54	0·57
Peroxide (1)	—	0·57	1·16	1·55	1·70	1·86	1·80	1·77	1·76	1·66
Peroxide (2)	—	—	0·08	0·16	0·20	0·31	0·48	0·30	0·27	0·20
$CH_3{\cdot}OH$	—	—	Trace	0·62	0·82	0·82	0·74	0·99	0·99	1·07
CO_2	—	0·07	0·38	0·76	1·08	1·31	1·43	1·66	1·76	2·04
CO	—	0·07	0·22	0·25	0·33	0·37	0·46	0·54	0·63	0·76
$CH_3{\cdot}CHO/O_2$ used	—	1·32	0·84	0·77	0·64	0·50	0·60	0·50	0·70	0·72
CO/CO_2	—	1·00	0·58	0·33	0·31	0·28	0·32	0·32	0·33	0·37

* In this and all the other tables the amounts of reactants and products are recorded in terms of moles × 10^{-4} unless otherwise stated.

Attention may be directed to the relative proportions of peroxide (1) and acid found throughout the reaction. If the peroxide consisted solely of peracetic acid then the acid figure should equal or exceed the peroxide figure, as indeed was found by Hatcher, Steacie, and Howland (*loc. cit.*) and by Pease (*loc. cit.*), who took the difference to be a measure of the acetic and formic acids present. In our experiments we were unable to detect any acetic or formic acid in the products immediately after cooling; and, in order to investigate the matter further, we repeated one of Pease's experiments in which an equimolecular acetaldehyde–oxygen mixture reacted at 100° and 40·2 cm. pressure, in a Pyrex glass bulb. The analysis again revealed a large excess of peroxide (1) over acid. It was observed, however, that the composition of the aqueous solution of products changed rapidly on standing, the acid content increasing by more than 100% in the course of an hour, whilst both the peroxide and aldehyde content diminished.

The data for two experiments are summarised in Table II. Since the residual aldehyde decreases to a much greater extent than the peroxide, it must be assumed that the latter consists of a mixture of peracetic acid (the quantity of which is given by the immediate acid titration) and another, isomeric, non-acidic peroxide which, on standing, may either change into peracetic acid or combine with the residual aldehyde to give acetic acid. If the increase in the acid content is assumed to be due to these changes, then a simple calculation gives the fraction (*k*) of the non-acidic peroxide changing into per-acid during the intervals of standing. The values of *k* are given in the last column of the table.

TABLE II.

Change in the composition of an aqueous solution of the products from the reaction of a CH_3·CHO + O_2 *mixture at* 100° *and* 40·2 *cm.*

	Time interval before analysis (mins.).	Products.			
		Acid.	Peroxide (1).	Residual CH_3·CHO.	*k*.
*	Immediate	6·08	13·71	15·80	—
	40	13·46	13·70	9·88	0·19
	60	16·50	11·90	9·86	0·59
†	Immediate	6·69	13·33	15·10	—
	35	14·00	13·10	9·34	0·23
	65	18·00	10·60	8·35	0·69

* Pressures recorded by mercury manometer.

† Mercury manometer replaced by Bourdon gauge.

(b) *The low-pressure ignition peninsula* (Table III). At 237° ignition is preceded by an induction period of about 20 secs. Samples taken during this period show that peroxide (1) is the principal product; just before ignition about 40% of the carbon of the aldehyde burnt is present in the system as peroxide (1), and 70—80% of the reactants remain uncombined. The ratio of aldehyde to oxygen consumed during the pre-ignition period is 1·4 and the ratio CO/CO_2 is 7·0. No methyl alcohol and only a trace of peroxide (2) are found, showing that little or no decomposition of peroxide (1) has taken place.

The products after ignition consist only of the two oxides of carbon, hydrogen, methane, and steam.

TABLE III.

Products from the combustion of an 18·8% CH_3·CHO–81·2% ($2N_2 + O_2$) *mixture in the low-temperature ignition peninsula.* $T = 237°$. $P = 16·7$ cm.

Time (secs.).	0.	10.	17.	After ignition.
CH_3·CHO	5·51	4·13	3·83	—
O_2	7·92	7·36	6·75	0·47
Acids	—	—	0·24	—
Peroxide (1)	—	0·15	0·50	—
Peroxide (2)	—	—	Trace	—
CO_2	—	0·02	(0·18)	2·84
CO	—	0·14	0·18	6·80
CH_4	—	—	—	0·30
H_2	—	—	—	3·25
CH_3·CHO/O_2 used	—	1·40	1·40	—
CO/CO_2	—	7·00	—	2·40

TABLE IV.

Products from the combustion of an 18·8% CH_3·CHO–81·2% ($2N_2 + O_2$) *mixture in the lower cool-flame zone.* $T = 245°$. $P = 16·5$ cm.

Time (secs.).	0.	6.	7.*	30.	60.
CH_3·CHO	5·36	3·92	2·03	2·05	2·25
O_2	7·72	6·98	4·85	4·60	4·38
Peroxide (1)	—	0·35	Trace	Trace	0·07
Peroxide (2)	—	—	0·15	0·18	0·14
H·CHO	—	—	0·26	0·35	0·39
CH_3·OH	—	—	1·65	1·65	1·98
CO_2	—	0·14	0·79	0·81	0·77
CO	—	0·23	2·82	2·84	2·81
CH_3·CHO/O_2 used	—	1·94	1·16	1·06	0·94
CO/CO_2	—	1·60	3·60	3·50	3·60

* Immediately after passage of cool flame.

(c) *The single cool-flame zone* (Table IV, Fig. 2). At 245° the induction period before the passage of the cool flame is 6·5 secs., and only permits of one sample being taken. The data show that just prior to inflammation, the conditions are not unlike those at the corresponding time before low-pressure ignition. Rather less of the reactants have combined and there is a smaller concentration of peroxide (1) in the medium. The ratio of aldehyde to oxygen consumed is 1·94.

During the passage of the cool flame, peroxide (1) is completely decomposed, giving methyl alcohol and small quantities of peroxide (2), and the rate of oxidation of the aldehyde is greatly increased. No acids are found at any stage of the reaction and hence, under the experimental conditions, peracetic acid is not formed. Formaldehyde is found in the medium after the passage of the cool flame and increases in quantity as the reaction proceeds; its presence constitutes the first evidence that the oxidation follows a different course from that at lower temperatures.

The ratio $CH_3 \cdot CHO/O_2$ falls to 1·16 and the ratio CO/CO_2 rises to 3·6 after the passage of the flame, the increase in the carbon monoxide content of the products being due in part to the decomposition of peroxide (1).

(d) *The double cool-flame zone.* At 300° there are two cool flames, the first appearing after an induction period of only 2 secs. and the second after 8·5 secs. The analytical results are very similar to those for a single flame and need not be given in detail. It may be mentioned, however, that the intensity of the second cool flame is less than that of the first, probably owing to the fact that peroxide (1), which disappears during the passage of the first flame, has not time to build up to the same concentration before the second inflammation occurs. Formaldehyde and peroxide (2) are present after the passage of the first flame and increase in amount as reaction proceeds. No per-acids or acids are formed and, even after the second flame has traversed the medium, nearly 40% of the original oxygen and 18% of the acetaldehyde remain uncombined.

(e) *The upper slow-combustion zone* (Table V). The reaction at 350° proceeds rapidly, nearly 80% of the aldehyde being used in the first 10 secs. No peroxide (1) survives in the products, but methyl alcohol and peroxide (2), arising from its thermal decomposition, are present in comparatively large amounts. Formaldehyde is also found throughout. The ratio $CH_3 \cdot CHO/O_2$ used is 1·08, and the ratio CO/CO_2 after 10 secs. is 5·50.

TABLE V.

Products from the combustion of an 18·8% $CH_3 \cdot CHO$–81·2% $(2N_2 + O_2)$ *mixture in the upper slow-combustion region.* $T = 350°$. $P = 16·6$ cm.

Time (secs.).	0.	5.	10.	Time (secs.).	0.	5.	10.
$CH_3 \cdot CHO$	4·50	0·95	0·61	CO_2	—	0·61	0·75
O_2	6·48	3·10	2·90	CO	—	3·71	4·10
Peroxide (2)	—	0·19	—	$CH_3 \cdot CHO/O_2$ used...	—	1·04	1·08
$CH_3 \cdot OH$	—	1·49	2·10	CO/CO_2	—	6·10	5·50
H·CHO	—	0·26	0·26				

Propaldehyde.—The products from a 12·55% propaldehyde in $(2N_2 + O_2)$ mixture were examined along the 28 cm. isobar (Part I, Fig. 2), at 235° (lower slow-combustion zone), 260° (lower cool-flame zone), and 360° (upper slow-combustion zone). The results, summarised in Tables VI—VIII, show a general resemblance to those of acetaldehyde and need not be commented on in detail. Attention may, however, be directed to certain features of importance in connection with the mechanism of the combustion.

(a) *The lower slow-combustion zone* (Table VI). During the course of the slow reaction, peroxide (1) and the acid figure reach a maximum when about one-half the reactants have been used. Peroxide (2), methyl alcohol, and formaldehyde, on the other hand, increase throughout. Ethyl alcohol is found in comparatively large quantities in the early stages of the reaction, but undergoes further rapid oxidation and cannot be detected in the later stages.

The ratio of propaldehyde to oxygen consumed falls from 1·14 after 20 secs. to 0·43 after 200 secs., when some 45% of the reactants still remain uncombined. This figure is lower than the corresponding ratio for acetaldehyde, possibly owing to the inclusion under propaldehyde of any acetaldehyde formed during the reaction.

(b) *Lower cool-flame zone* (Table VII). Two analyses were carried out at 260°, one immediately before and the other after the passage of a cool flame. On comparing the results with those for acetaldehyde (Table IV), it will be seen that the ratio of aldehyde to oxygen used falls rapidly after the passage of the flame, and the ratio CO/CO_2 is much greater than for the slow-combustion zone. Peroxide (1) is found in the pre-flame period, and peroxide (2) after the passage of the flame.

Table VI.

Products from the combustion of a 12·55% $C_2H_5\cdot CHO$–87·45% $(2N_2 + O_2)$ *mixture in the lower slow-combustion region.* $T = 235°$. $P = 28·1$ cm.

Time (secs.).	0.	20.	40.	60.	80.	100.	140.	200.
$C_2H_5\cdot CHO$ *	6·22	4·96	3·64	3·78	2·75	2·85	2·76	2·60
O_2	14·43	13·33	12·09	9·58	8·60	7·94	7·00	6·02
Acids	—	0·12	0·28	0·37	0·37	0·38	0·39	0·33
Peroxide (1)	—	0·25	0·75	1·16	1·17	1·18	1·24	1·04
Peroxide (2)	—	0·06	0·20	0·40	0·59	0·66	0·75	0·84
$CH_3\cdot OH$	—	0·74	0·83	0·86	1·23	1·62	1·90	2·11
$C_2H_5\cdot OH$	—	0·58	0·50	0·72	0·41	—	—	—
$H\cdot CHO$	—	—	0·12	0·32	0·41	0·50	0·54	0·54
CO_2	—	0·17	0·46	1·06	1·42	1·70	2·09	2·77
CO	—	0·47	0·84	1·22	1·66	1·98	2·25	2·77
$C_2H_5\cdot CHO/O_2$ used *	—	1·14	1·10	0·50	0·59	0·54	0·47	0·43
CO/CO_2	—	2·80	1·80	1·14	1·20	1·16	1·08	1·00

* Including any acetaldehyde.

Table VII.

Products from the combustion of a 12·55% $C_2H_5\cdot CHO$–87·45% $(2N_2+O_2)$ *mixture in the lower cool-flame zone.* $T = 260°$. $P = 27·0$ cm.

Time (secs.).	0.	6.	8.*
$C_2H_5\cdot CHO$	5·69	3·98†	2·54†
O_2	13·20	12·60	9·92
Peroxide (1)	—	0·10	Trace
Peroxide (2)	—	Trace	0·49
$CH_3\cdot OH$	—	1·43	1·34
$H\cdot CHO$	—	—	0·54
CO_2	—	0·08	0·48
CO	—	0·32	2·72
C_2H_4	—	—	0·48
$C_2H_5\cdot CHO/O_2$ used*	—	2·85	0·96
CO/CO_2	—	4·00	5·70

* After passage of flame.
† Including acetaldehyde.

Table VIII.

Products from the combustion of a 12·55% $C_2H_5\cdot CHO$–87·45% $(2N_2 + O_2)$ *mixture in the upper slow-combustion region.* $T = 360°$. $P = 28·0$ cm.

Time (secs.).	0.	5.	10.
$C_2H_5\cdot CHO$	4·97	0·92*	1·09*
O_2	11·53	6·95	6·30
Peroxide (2)	—	0·35	0·45
$H\cdot CHO$	—	0·54	0·54
$CH_3\cdot OH$	—	1·31	1·55
CO_2	—	0·51	0·74
CO	—	4·71	7·51
C_2H_4	—	1·06	1·49
$C_2H_5\cdot CHO/O_2$ used *	—	0·88	0·74
CO/CO_2	—	9·25	10·00

* Including any acetaldehyde.

(c) *Upper slow-combustion zone* (Table VIII). At 360° no peroxide (1) or ethyl alcohol survives in the products, but methyl alcohol, peroxide (2), and formaldehyde are found in considerable quantities. The ratio propaldehyde to oxygen used is 0·74 after 10 secs. when about one-half the oxygen has been consumed.

(With V. V. Kelkar.) *Glyoxal* (Table IX).—Qualitative analysis of the oxidation products of glyoxal gave peroxides, formaldehyde, oxalic acid, the two oxides of carbon, and steam. Glyoxylic acid was not detected. In this respect our results differ from those of Steacie, Hatcher, and Horwood (*loc. cit.*), who found no oxalic acid but considerable quantities of glyoxylic acid. Their experiments, however, were carried out at 150—220°, whereas we have worked at 350° and upwards, under conditions approaching ignition.

Quantitative analyses were carried out at two points on the 12 cm. isobar (Part I, Fig. 7), at 350° (adjacent to the low-pressure ignition boundary) and at 515°, and a third at 515° and 21 cm. (adjacent to the high-temperature ignition boundary).

Table IX.

Products from the slow oxidation of a $(CHO)_2 + O_2 + N_2$ *medium at* 350° *and* 515°.

		Products, as moles × 10^{-2}.				
Temp.	Press., cm.	CO_2.	CO.	Peroxide.	Oxalic acid.	CO/CO_2.
350°	12	1·04	4·67	0·25	0·49	4·50
515	12	4·63	2·52	—	0·05	0·54
515	21	6·93	4·32	0·03	0·12	0·62

It will be noted that, in both instances in which combustion takes place near the ignition curve, peroxides survive in the products together with comparatively large quantities of oxalic acid.

Acraldehyde (Table X).—The products from a 50% acraldehyde in oxygen mixture were examined at 240° (lower slow-combustion zone; see Part I, Fig. 8), and those from a CH_2:CH·CHO + O_2 + N_2 mixture at 325° (cool-flame zone), and at 350° (upper slow-combustion zone).

TABLE X.

Products from the combustion of acraldehyde at 240°, 325°, *and* 350°.

Reacting mixture		CH_2:CH·CHO + O_2				CH_2:CH·CHO + O_2 + N_2	
Temperature		240°				325°	350°
Pressure, cm.		20				10·3	10·3
		Reactants and products as moles × 10^{-2}.					
Time (mins.)	0	2·45	5·33	8·46	23·25	—	—
Reactants :							
CH_2:CH·CHO	16·3	11·53	9·46	8·10	4·92	4·8	4·6
Oxygen	16·3	15·21	3·96	0·15	0·10	4·8	4·6
Products :							
Acids	—	1·85	5·02	3·37	3·65	0·28	0·20
Peroxides	—	0·23 *	1·50	0·68	0·15	0·14 †	0·06
H·CHO	—	1·47	2·94	2·79	2·64	0·74	0·88
CO_2	—	2·34	6·65	8·22	7·81	2·07	1·74
CO	—	3·99	9·74	12·40	13·53	4·89	4·88
C_2H_4	—	—	—	—	—	0·22	0·25
CO/CO_2	—	1·71	1·46	1·51	1·73	2·4	2·8

* Trace of ethylene oxide. † Considerable ethylene oxide.

Owing to the milder character of the processes occurring at low temperatures, the distinction between the cool-flame and the slow-combustion zones is not so marked as in the case of the saturated aldehydes. At 240° and 20 cm. the peroxides, acids, and formaldehyde reach a maximum after 5 mins., when 75·8% of the oxygen has been used up.

At 325° and 10·3 cm., in the cool-flame zone, and at 350° in the upper slow-combustion zone, the amounts of condensable products surviving are considerably less than in the lower slow-combustion zone, and the CO/CO_2 ratio is greater. There is also evidence of some thermal decomposition of the aldehyde in this region; *e.g.*, ethylene appears in the gaseous products, and a considerable amount of ethylene oxide, formed by its further oxidation, is found.

DISCUSSION.

Although analytical results cannot of themselves reveal the mechanism of a chain-branching process which probably involves radicals, yet they may afford a valuable guide to the course of the reaction by establishing the various steps leading to the formation of stabilised intermediate products.

In discussing the results of the present work the principal points requiring consideration are (*a*) the nature of peroxides (1) and (2), (*b*) the reactions leading to the formation of alcohols and lower aldehydes, (*c*) the occurrence of per-acids and acids, and (*d*) the conditions leading to cool flame and normal ignition in the low-temperature region. It is proposed to deal with glyoxal and acraldehyde in a further communication.

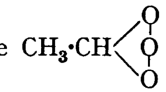
The view generally held as to the mechanism of aldehyde oxidation is that reaction must be preceded by an activation of the aldehyde which then combines with oxygen to give an active peroxide; the latter, by loss of energy in a subsequent collision changes to the corresponding isomeric per-acid. Evidence in support of this mechanism, which was first suggested by Bodenstein (*loc. cit.*), and later modified by Bäckström (*Z. physikal. Chem.*, 1934, *B*, **25**, 99), has been obtained by Pease, Hatcher, Steacie, and Howland and others (*loc. cit.*), working with acetaldehyde and propaldehyde in the lower slow-combustion zone. Pope, Dykstra, and Edgar (*loc. cit.*), working with higher aldehydes in and near the cool flame zone, concluded that oxidation proceeds *via* a series of lower aldehydes and does not require the intervention of peroxides or per-acids.

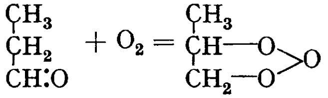
Our results cannot be said to support either view, for although we have detected at least two types of peroxide in the products, we have obtained no evidence of the presence of per-acids or acids in the medium during reaction except at low temperature, although both appear to be formed in an aqueous solution of the products containing an excess of the aldehyde. Lower aldehydes have been detected, in certain circumstances, but appear to be formed by a secondary oxidation favoured by high temperatures. Further experiments are being undertaken to ascertain if this reaction occurs preferentially with higher members of the series.

Clover and Houghton's method of estimating peroxides (*loc. cit.*) distinguishes between two types, *viz.*, those which liberate iodine rapidly from neutral potassium iodide solution (*e.g.*, per-acids) and those which liberate it slowly from acid potassium iodide (*e.g.*, alkyl peroxides). Both are present in the products from aldehyde oxidation.

Our results are best interpreted on the assumption that peroxide (1) is a comparatively stable non-acidic peroxide, which changes into per-acid in aqueous solution on standing. Thus, it has been shown that on arresting the oxidation at an early stage and dissolving the products in water, the solution at first contains a relatively large quantity of peroxide (1) and little per-acid or acid. On standing, out of contact with air, peroxide (1) changes into a per-acid, part of which combines with the excess aldehyde present to give the corresponding acid.

Peroxide (1) has not been isolated and its structure must, therefore, be a matter of conjecture. The analytical results, however, reveal some of its properties; in particular, it appears to decompose in the cool flame, and at high temperatures, to give an alkyl peroxide, an alcohol, and one or both oxides of carbon, whereas at low temperatures and in aqueous solution it is comparatively stable.

In the case of acetaldehyde Bodenstein has assigned the structure  $CH_3{\cdot}CH\langle\begin{smallmatrix}O\\|\\O\\|\\O\end{smallmatrix}$ to the initially formed activated peroxide. Such a compound, however, would hardly be expected to possess much stability, and in view of all the facts it seems more probable that peroxide (1) has an ozonide structure. According to this view the initial stage of the oxidation of propaldehyde would be



$$\begin{matrix}CH_3\\|\\CH_2\\|\\CH{:}O\end{matrix} + O_2 = \begin{matrix}CH_3\\|\\CH{-}O\\|\\CH_2{-}O\end{matrix}\!\!>\!O$$

The ozonide would then undergo rearrangement to give perpropionic acid which in turn would decompose into ethyl peroxide [peroxide (2)] or ethyl alcohol, as follows (Egerton and Harris, private communication):

$$\text{(i)}\quad CH_3{\cdot}CH_2{\cdot}C{<}\!\begin{smallmatrix}O\cdot OH\\O\end{smallmatrix} \longrightarrow CH_3{\cdot}CH_2{\cdot}O{\cdot}OH + CO$$

$$\text{(ii)}\quad CH_3{\cdot}CH_2{\cdot}C{<}\!\begin{smallmatrix}O\cdot OH\\O\end{smallmatrix} \longrightarrow CH_3{\cdot}CH_2{\cdot}OH + CO_2$$

The ratio of aldehyde to oxygen consumed in the various combustion zones shows that, in the absence of a large excess of oxygen, reaction does not go to completion. For instance, with acetaldehyde, in the initial stages when very little of the combustible has reacted, the ratio has a value approaching 2, pointing to some surface action; in the later stages it falls to about 0·7 in the lower slow-combustion zone and to 1 in the other zones. The experimental values are as follows:

	Ratio $CH_3{\cdot}CHO/O_2$.	
Reaction zone.	Initial.	Final.
Lower slow-combustion	1·32	0·84—0·72
Low-temperature ignition	1·40	—
Lower cool-flame	1·94	1·16—0·94
Upper cool-flame	—	1·06—0·93
Upper slow-combustion	—	1·04—1·08

It would, therefore, appear that above the lower slow-combustion zone, oxidation practically ceases with the formation of peroxide (1).

The analytical results throw some light on the changes occurring in the neighbourhood of the three pressure limits of acetaldehyde and propaldehyde. It is evident that in the lower slow-combustion zone, at 230°, the concentration of peroxide (1) in the medium at any instant is determined by the relative rates at which it is formed and decomposes (Table I). In the early stages of the reaction the rate of formation is the greater and the concentration builds up; but after about 2 mins. the two rates become equal and thereafter it decomposes faster than it is formed.

On increasing the temperature to 237° the concentration increases rapidly until it reaches a critical value at which explosive decomposition takes place with evolution of heat and light (cf. Harris and Egerton, *Proc. Roy. Soc.*, 1938, *A*, **168**, 1). This may well exert a trigger action and give rise to normal ignition. At higher temperatures the rate of decomposition would prevent the attainment of the critical explosion pressure, and the products of decomposition may then be supposed to furnish the active centres responsible for the chain processes occurring in the cool-flame zone.

In order to test these views, further information as to the effect of vessel diameter, diluents, and other factors on the limits is required.

The formation of lower aldehydes may be due, in part, to the interaction of peroxide (1) with steam, or to the decomposition of peroxide (2); but their concentration at high temperatures makes it more probable that they result from direct oxidation of the higher aldehyde, either by hydroxylation or according to the reactions suggested by Pope, Dykstra, and Edgar. This secondary oxidation, however, only takes place to a minor degree with acetaldehyde and propaldehyde.

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