473. *Oxidation of Aldehydes in the Gaseous Phase. Part I. Low-temperature Oxidation of Acetaldehyde.*

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The oxidation of acetaldehyde in the gas phase has been investigated at 120° and it is shown that it is a radical chain reaction, the rate of which is governed by the equation $-d[CH_3\cdot CHO]/dt = k[CH_3\cdot CHO]^2$. Nitrogen peroxide and *iso*propyl alcohol inhibit the oxidation but nitrogen has no effect on it. Increasing the surface-volume ratio by a factor of ten increases the rate of the reaction by about 60%. A reaction mechanism is proposed which accounts for the experimental observations.

The thermal oxidation of acetaldehyde in the gaseous phase was first investigated in detail by Bodenstein and his students (*Sitzber. preuss. Akad.*, Phys.-Math. Kl., 1931, III, 1; *Z. physikal. Chem.*, 1931, **12**, *B*, 151), who studied the reaction between 55° and 90°. At these temperatures there is a decrease in pressure as the reaction proceeds, and the main product is not acetic acid but peracetic acid. Bodenstein states that the reaction is characterised by long and irregular induction periods and that its rate is proportional to the square of the acetaldehyde concentration and inversely proportional to the oxygen concentration. In the light of these results Bodenstein put forward a mechanism which yielded an equation for the overall reaction in agreement with his experimental data. There were, however, many unsatisfactory features in this work, and the reaction was later investigated in greater detail by Hatcher, Steacie, and Howland (*Canadian J. Res.*, 1932, **7**, 149), who studied the reaction between 60° and 120° and carried out a fairly complete analysis of both liquid and gaseous products, and brought to light many interesting features. Their results agreed with Bodenstein's in showing that the rate of the reaction was approximately proportional to the square of the acetaldehyde concentration, but they found that it was uninfluenced by the oxygen concentration. They observed a slight induction period at the commencement of the reaction but it was very much smaller than those observed by Bodenstein, and for this reason they suggested that the irregular induction periods which he observed must have been due to impurities. Hatcher, Steacie, and Howland further differed from Bodenstein in stating that they found one of the reaction products to be formic acid. Though they were somewhat critical of Bodenstein's researches they agreed that the apparent activation energy for the reaction is about 10 kcals. and that the reaction is influenced by the surface of the reaction vessel.

This work of Hatcher, Steacie, and Howland is open to criticism on two points. First, they pre-mixed the acetaldehyde and the oxygen in the presence of mercury, a procedure which is objectionable for it is known that mercury catalyses the reaction between aldehydes and oxygen (Hatcher, Steacie, and Rosenberg, *J. Physical Chem.*, 1934, **38**, 1189); secondly, they used a mercury manometer to follow the course of the reaction. It has been shown on a number of occasions that one obtains erroneous results if a mercury manometer is used in the study of the oxidation of aldehydes (Snowden and Style, *Trans. Faraday Soc.*, 1939, **35**, 426; Newett, Baxt, and Kelkar, *J.*, 1939, 1703). This objection also applies to the work of Pease (*J. Amer. Chem. Soc.*, 1933, **55**, 2753) who later investigated the reaction at 120°. Pease did not pre-mix his gases and his results agree reasonably well with those of Hatcher, Steacie, and Howland, though he differed from them in one important aspect, namely, he did not find any carbon dioxide in his gaseous reaction products except when the reaction vessels were coated with potassium chloride. He found that the rate of the reaction was proportional to the square of the acetaldehyde concentration and uninfluenced by the oxygen concentration. He further showed that the oxidation is inhibited by ethyl alcohol vapour but uninfluenced by water vapour and nitrogen, and concluded that it was probably a chain reaction. Pease carried out a few experiments to investigate the effect of the surface-volume ratio on the rate of reaction and also studied the effect of coating the surface of the reaction vessel with potassium chloride. From these experiments he concluded that the chains probably started on the walls of the vessel and ended in the gas phase. Because of the differences in the experimental results of these various workers, we have re-examined this reaction. Further, a knowledge of the mechanism of the oxidation of acetaldehyde is important in the study of the oxidation of organic compounds in general and it seemed desirable to attempt to discover the mechanism by which this reaction occurred.

In this investigation we have avoided the use of mercury manometers for pressure measurements and have taken considerable care to purify our acetaldehyde and oxygen. We have also analysed the liquid reaction products immediately after an experiment for it has been shown that erroneous results are obtained unless the mixture of acids and unchanged aldehyde is analysed without delay.

EXPERIMENTAL.

Apparatus.—The general apparatus assembly was of the conventional high-vacuum type, the reaction vessel being made from Pyrex tubing of 40 mm. diameter. The volume was determined experimentally as 214·6 c.c. The temperature of the electric furnace could be controlled to ±0·2° by means of a " Sunvic " energy regulator. The rate of the reaction was followed by observing the pressure change by either a glass " Bourdon " type manometer or a metal bellows manometer of the type described by East and Kuhn (*J. Sci. Instr.*, 1946, **23**, 185). Both these manometers were used as null instruments and it was found that reproducible results were obtained when the gauges were interchanged.

As the reaction was very sensitive to surface impurities, great care had to be taken in cleansing the vessel. This was usually done by filling it with chromic acid and setting it aside, and then rinsing it with water for several hours. It was then sealed in position, and evacuated and baked in the furnace for several hours. Several trial runs had to be made until reproducible results were obtained.

Materials.—The acetaldehyde was purified by distilling the "pure" commercial product in an atmosphere of nitrogen, and dried by passing the vapour over calcium chloride. It was then redistilled several times in a vacuum, being condensed each time at −80° in a " cardice "–acetone cooled trap. It was stored in a darkened vessel closed by a metal needle-valve, as it had been found that traces of tap grease appeared to accelerate the polymerisation of the acetaldehyde.

The oxygen was prepared by electrolysis of sodium hydroxide and freed from hydrogen by passing it over heated platinised asbestos, and from carbon dioxide by " Carbosorb." It was dried by passing it over phosphoric oxide.

The *iso*propyl alcohol was purified and freed from acetone by heating it under reflux for 3 or 4 hours with 2 : 4-dinitrophenylhydrazine, and then fractionating it in a stream of nitrogen. It was then distilled under vacuum and stored under its own vapour.

Nitrogen peroxide was prepared by heating lead nitrate in a stream of oxygen. The product was passed over phosphoric oxide and condensed in a trap at −80°. It was purified by several distillations under vacuum and stored in solid form at −80° until required.

Analysis of Products.—The reaction products were removed from the vessel by means of a Töpler pump through a trap at −80°. The non-condensable gases were collected over mercury, and their volume determined. Aliquot portions were then analysed for residual aldehyde, residual oxygen, carbon monoxide, carbon dioxide, and hydrocarbons by means of a modified Bone–Newitt gas-analysis apparatus. The condensable material in the −80° trap was dissolved in water and analysed as follows. A portion was titrated with N/100-potassium hydroxide using phenolphthalein as indicator; this gave the total carboxylic acids. A second portion was analysed for peroxide by adding a known volume of standard hydrochloric acid and excess of potassium iodide, the liberated iodine being titrated with N/100-sodium thiosulphate solution. Phenolphthalein was then added, and the residual acid determined by titration with N/100-potassium hydroxide. Only acyl peroxides and hydrogen peroxide react immediately with acidified potassium iodide to liberate iodine, so the above method yields the amount of peracetic acid or hydrogen peroxide in our condensable reaction products. Peracetic acid and hydrogen peroxide react with the above reagents as follows :

$$CH_3{\cdot}CO_3H + HCl + 2KI = CH_3{\cdot}CO_2K + KCl + H_2O + I_2$$
$$H_2O_2 + 2HCl + 2KI = 2KCl + 2H_2O + I_2$$

Since in both cases 2 equivs. of acid are necessary to produce 2 equivs. of iodine it is impossible by this method to determine the two peroxides separately, but the fact that the total peroxides given by this method sometimes exceeded the total carboxylic acids in the condensable reaction products must mean that some hydrogen peroxide was also produced as this is the only ***neutral*** peroxide which reacts with acidified potassium peroxide as rapidly as peracetic acid. A third portion was analysed for unchanged acetaldehyde by adding excess of hydroxylamine hydrochloride and titrating the liberated acid with N/100-potassium hydroxide using bromophenol-blue as indicator.

Experimental Results.

A typical pressure–time curve for the reaction at 120° is shown in Fig. 1: after a brief induction period, the pressure decreases steadily and at a uniform rate over the major part of the reaction. Towards the end of the reaction there is a decrease in the rate of pressure charge and finally the pressure increases slightly. By choosing the acetaldehyde and oxygen concentrations to correspond with one of Pease's (*loc. cit.*) experiments we found that our pressure–time curve agreed with his results for a vessel of similar dimensions. Pease observed this increase of pressure towards the end of the reaction but did not investigate it. We have carried out some runs at higher temperatures and found that this increase in pressure after the minimum pressure was more pronounced and must be attributed to the thermal decomposition of either peracetic acid or the peracetyl radical (see following paper).

FIG. 1.

Typical reaction curve.

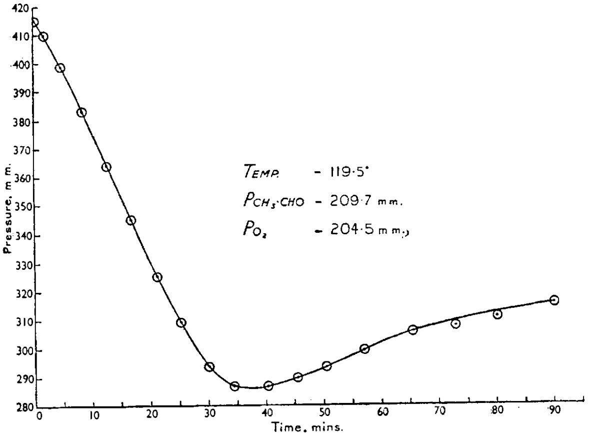
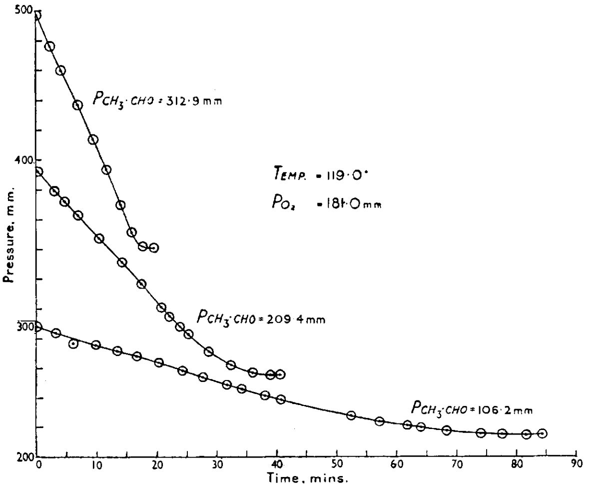


FIG. 2.

Effect of variation in aldehyde concentration.



Throughout this investigation we found that the slight induction period at the commencement of the reaction was reproducible. In general, the reaction was stopped at the point where no further decrease in pressure occurred, and the mixture was pumped off and analysed. For a few mixtures, however, we made analyses at different intervals throughout the whole reaction in order to see how the yield of products varied during the course of the reaction.

Effect of Aldehyde Concentration.—The effect of acetaldehyde concentration on the rate of reaction was investigated by varying the acetaldehyde concentration while keeping that of the oxygen constant. The pressure–time curves for three runs are shown in Fig. 2, and in the following table we give the time (t_{10-60}) required for the pressure to drop from 10 to 60 mm. below the original value. It will be observed that an increase in the acetaldehyde concentration produces a marked increase in the rate of the reaction. By plotting the logarithm of $1/t_{10-60}$ against the logarithm of the aldehyde concentration a straight line was obtained. From the slope of this graph we find that the rate varies as $A^{1.87}$ at 120°. This is in good agreement with the value obtained by Hatcher, Steacie, and Howland (*loc. cit.*) though slightly lower than the value of 2 obtained by Pease.

Variation of rate of reaction with acetaldehyde concentration.

Aldehyde, mm. Hg	312·9	209·4	106·2
O_2, mm. Hg	182·8	180·7	180·0
t_{10-60}, mins.	5·6	11·6	42·6

FIG. 3.

Effect of variation in oxygen concentration.

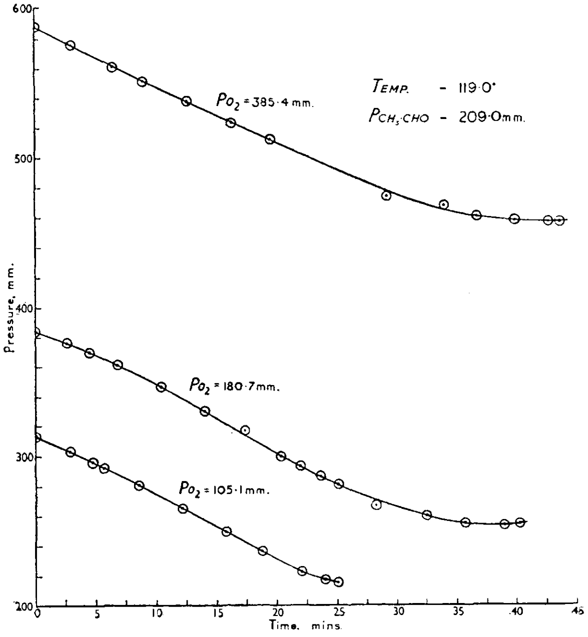
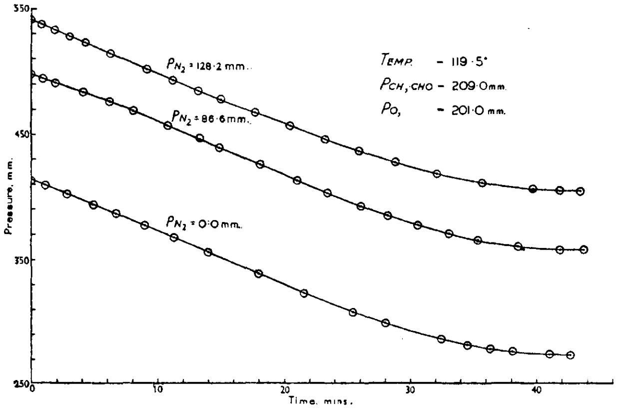


FIG. 4.

Effect of nitrogen.



Effect of Oxygen Concentration.—In a similar manner by varying the oxygen concentration while keeping the acetaldehyde concentration constant it was found that oxygen had little effect on the reaction rate over a wide range of concentration change. The pressure–time curves are shown in Fig. 3, and below we give the values of t_{10-60} for the various oxygen concentrations.

Effect of oxygen concentration on rate of reaction.

Oxygen, mm. Hg	385·4	180·7	105·1
Acetaldehyde, mm. Hg	202·7	209·4	209·4
t_{10-60}, mins.	12·6	11·6	11·8

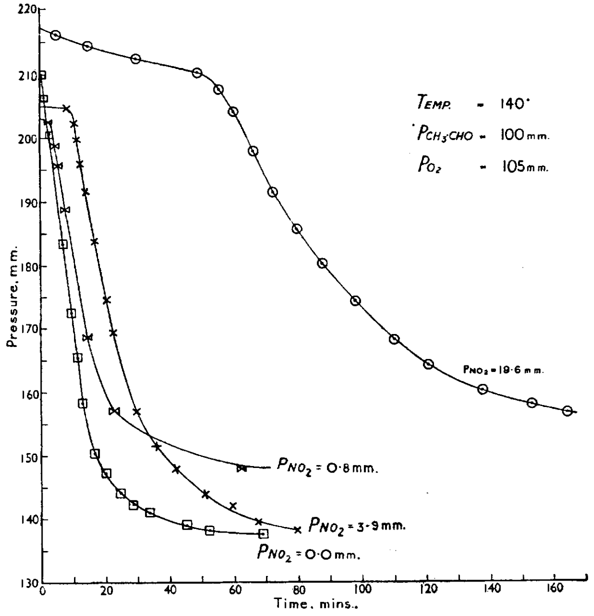
These results are in agreement with the negligible effect of oxygen concentration on the maximum rate of reaction as found by Hatcher, Steacie, and Howland (*loc. cit.*) and by Pease (*loc. cit.*), but in disagreement with Bodenstein's work which showed that the reaction was inhibited by oxygen.

Effect of Inert Gases.—The effect of inert gas was investigated by adding varying amounts of nitrogen to a given acetaldehyde–oxygen mixture. The following table gives the results of the experiments, and the pressure–time curves are shown in Fig. 4. These show clearly that the rate of the reaction is uninfluenced by inert gases.

Acetaldehyde, mm. Hg	209·5	208·9	209·5
Oxygen, mm. Hg	200·9	199·7	201·9
Nitrogen, mm. Hg	128·2	86·6	0
t_{10-60}, mins.	12·2	12·6	11·8

FIG. 5.

Effect of nitrogen peroxide.



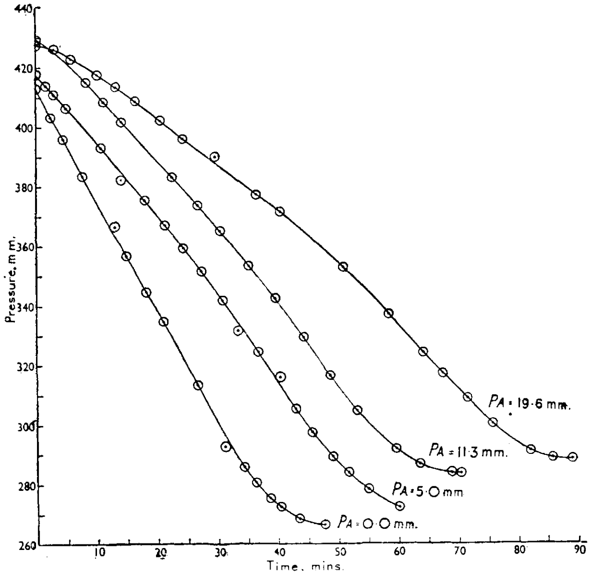
Effect of Inhibitors.—Pease found that the reaction was inhibited by ethyl alcohol vapour but not by water vapour and so concluded that the oxidation was a chain reaction. Kane (*Proc. Roy. Soc.*, 1939, **171**, *A*, 251), while investigating the explosive reaction between oxygen and acetaldehyde, found that nitrogen peroxide lengthened the induction period. It is well known that nitrogen peroxide can act as an inhibitor or as a sensitiser of explosions depending on the quantity present (Norrish and Griffith, *ibid.*, 1933, **139**, *A*, 147), but even at quite small concentration Kane still observed that the induction period was lengthened by the presence of nitrogen peroxide. We investigated the effect of nitrogen peroxide and *iso*propyl alcohol vapour on the slow oxidation of acetaldehyde and found that both inhibit the reaction. However, they seem to act by different mechanisms. The pressure–time curves at 140° for a given mixture of oxygen and acetaldehyde with different amounts of nitrogen peroxide are shown in Fig. 5, and similar curves at 120° for inhibition by *iso*propyl alcohol are shown in Fig. 6. It will be observed that with nitrogen peroxide the induction periods are considerably lengthened, whereas *iso*propyl alcohol has little effect on the initial stages of the reaction and it seems mainly to affect the general overall rate of reaction.

Effect of Temperature.—Two mixtures of acetaldehyde and oxygen were investigated at different temperatures in order to determine the activation energy of the reaction. A plot of the logarithm of $1/t_{10-60}$ against $1/T$ gave 13·96 and 14·6 kcals. for the activation energy of the reaction, both somewhat higher than the values of 10 kcals. given by Bodenstein and 8·7 kcals. given by Hatcher, Steacie, and Howland.

Effect of Surface/Volume Ratios.—The surface/volume ratio was increased ten-fold by packing the reaction vessel with lengths of 2-mm. Pyrex capillary tubing. A mixture containing 212·5 mm. of acetaldehyde and 200 mm. of oxygen was allowed to react at 120° and 131°. Reproducible results were obtained after a few preliminary runs, and the vessel was then detached from the reaction system, the capillary tubes removed, the vessel replaced, and the rate of the reaction measured. A ten-fold increase in the surface/volume ratio only increased the rate of reaction by about 60%. The relevant figures are given in the following table.

FIG. 6.

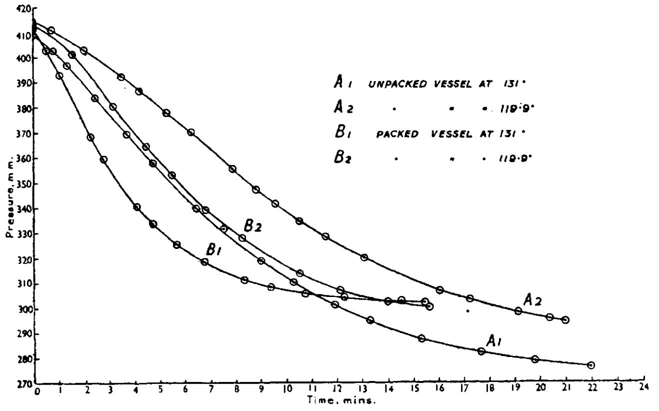
Effect of iso*propyl alcohol.*



Temp., 120°. P_{O_2} = 200 mm. (approx.). $P_{CH_3 \cdot CHO}$ = 210 mm. P_A = pressure of *iso*propyl alcohol.

FIG. 7.

Effect of increasing surface.



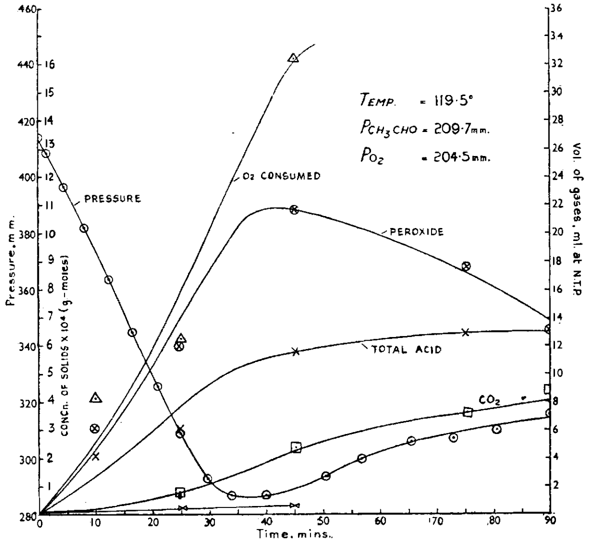
Effect of varying surface/volume ratio.

Surface/volume ratio.	Temp.	t_{10-60}.	Ratio.	Surface/volume ratio.	Temp.	t_{10-60}.	Ratio.
15·28	120°	4·14	1·5	15·28	131°	2·63	1·7
1·46	120	6·23		1·46	131	4·47	

Course of the Reaction.—A series of runs were done at 119·5° with a mixture of constant composition, *viz.*, 209·7 mm. of acetaldehyde and 204·5 mm. of oxygen. The reaction was stopped at intervals, and the products pumped off and analysed. The results are shown in Fig. 8 together with the pressure–time curve for this particular mixture. There are many interesting features in these results. First, we see clearly that the main condensable products of the oxidation are peroxides, and further that carbon monoxide and dioxide are produced throughout the reaction in agreement with the work of Bodenstein, and of Hatcher, Steacie, and Howland but contrary to the findings of Pease. It will also be noted that the maximum yield of peroxides corresponds with the minimum in the pressure–time curve and that as the pressure starts to increase the yield of peroxide decreases, but the amount of carbon dioxide produced commences to increase. During this period there is practically no increase in the total amount of carboxylic acids; hence, we must conclude that the increase of pressure after the minimum is due to the decomposition of the peracetic acid or the peracetyl radical, this decomposition yielding an acid as one of its products. Another interesting feature is that the amount of peroxide produced throughout most of the reaction is greater than the amount of total carboxylic acids. Newitt, Baxt, and Kelkar (*loc. cit.*) also noted that in their experiments excess of peroxide was produced, but Pease seems never to have observed an excess, possibly owing to a delay in analysis of the products.

FIG. 8.

Course of reaction.



(The lowest line refers to CO.)

It was pointed out earlier that hydrogen peroxide is the only *neutral* peroxide which reacts with acidified potassium iodide as rapidly as peracetic acid, and so it seems that our results must mean that it is produced in this oxidation.

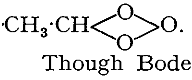
DISCUSSION.

The experimental results given above all point to this oxidation being a chain reaction, and the inhibition by *iso*propyl alcohol and nitrogen peroxide suggests that the mechanism is probably a free-radical one. The pressure–time curves are of the type usually encountered in autoxidation processes, which are now agreed to be controlled by free-radical mechanisms. Our experiments show clearly that the rate of this low-temperature oxidation of acetaldehyde is given by the expression $R = k[A]^n$, where n is approximately 2. We shall confine our remarks here to the portion of the pressure–time curves from the commencement of the reaction to the minimum, for, as shown above, this region corresponds to the oxidation of the acetaldehyde. The rise in pressure after the minimum is clearly due to the decomposition of peracetic acid or the peracetyl radical and will be discussed later (see following paper).

Bodenstein originally put forward a thermal-chain mechanism to account for his experimental results. His mechanism was:

$A = A^*$ . . . . (1)
$A^* + O_2 = P^*$ . . . . (2)
$P^* + A = P + A^*$ . . (3)
$P^* + O_2 = P + O_2$ . . . . . . (4)
$P^* + \text{wall} = P$ . . . . (5)

This mechanism leads to the kinetic expression $d[P]/dt = k[A]^2/([O_2] + 150)$. Later, Bodenstein (*Z. physikal. Chem.*, 1931, **12**, *B*, 153) identified A with the acetyl radical and P with


$CH_3{\cdot}CH{<}^{O}_{O}{>}O$.

Though Bodenstein later (*Rec. Trav. chim.*, 1940, **59**, 48) modified his ideas slightly by adopting a general free-radical scheme, he again put forward essentially the same mechanism.

It should be noted that the photochemical oxidation of acetaldehyde has been shown to be a chain reaction (Bowen and Tietz, *J.*, 1930, 234; Carruthers and Norrish, *J.*, 1936, 1036).

A satisfactory mechanism for the photo-oxidation of acetaldehyde was first given by Bäckström (*Z. physikal. Chem.*, 1934, *B*, **25**, 115). In this mechanism it is assumed that the chains are propagated by the reactions :

$$CH_3{\cdot}CO + O_2 = CH_3{\cdot}CO_3 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

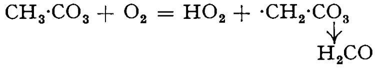
$$CH_3{\cdot}CO_3 + CH_3{\cdot}CHO = CH_3{\cdot}CO_3H + CH_3{\cdot}CO \quad . \ . \ . \ . \ . \ . \quad (3)$$

This suggestion has been utilised by Ubbelohde (*Proc. Roy. Soc.*, 1935, *A*, **152**, 382) in his theory of hydrocarbon oxidation, and more recently by Hinshelwood and his co-workers (Labile Molecule Discussion, Faraday Society, 1947, p. 117). Lewis and von Elbe ("Combustion, Flames and Explosions of Gases," Cambridge, 1938) and Bodenstein (*Rec. Trav. chim.*, 1940, **59**, 48) have also adopted it in their discussion of the oxidation of acetaldehyde, the former observing that it is the simplest and most direct route by which one could conceive peracetic acid being formed from acetaldehyde.

We are of the opinion that the above reactions are, in fact, those by which peracetic acid is formed in the gas-phase oxidation of acetaldehyde; and we assume that the acetyl radical is produced initially by the reaction :

$$CH_3{\cdot}CHO + O_2 = CH_3{\cdot}CO + HO_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

Such a reaction is the most direct way by which acetyl radicals could be formed from acetaldehyde and, though there has in the past been little experimental evidence for the stability of the HO_2 radical, yet it has recently been detected during a mass-spectrometric study of the oxidation of propane (Eltenton, *J. Chem. Physics*, 1947, **15**, 478). By the inclusion of such an initiation process we are able to explain certain of our experimental observations. Whatever may be the fate of the perhydroxyl radical (HO_2), one would expect that hydrogen peroxide would be produced. This is in agreement with our analyses, which suggest that hydrogen peroxide is formed during this oxidation. Examination of Fig. 8, however, shows that the rate of production of peroxides is greater than the rate of production of acids, *i.e.*, it suggests that there must be some terminating reaction which is also giving hydrogen-peroxide or its precursor. Thus we are lead to postulate that the terminating process is *



$$\begin{array}{l} CH_3{\cdot}CO_3 + O_2 = HO_2 + {\cdot}CH_2{\cdot}CO_3 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad H_2CO + CO_2 \end{array} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

This reaction accounts for the production of carbon dioxide in the oxidation, and also for formaldehyde, which has been found to be a product of the oxidation of all higher aldehydes (Ubbelohde, *loc. cit.*; Egerton, Smith, and Ubbelohde, *Phil. Trans.*, 1934, **A**, **234**, 484; Jost, "Explosions- und Verbrennungs-vorgänge in Gasen," Berlin, 1939, p. 534). In the oxidation of acetaldehyde, carbon dioxide is always produced in much greater quantity than the monoxide; this suggests that the latter is formed by a reaction aside from the main chain. Since small quantities of hydrocarbons are also produced, we suggest that they and the carbon monoxide arise from the decomposition of a small proportion of the acetyl radicals, *viz.* :

$$CH_3{\cdot}CO = CH_3 + CO \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$2CH_3 = C_2H_6,\ \text{etc.} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

Bawn and Tipper (Labile Molecule Discussion, Faraday Society, 1947, p. 103) have shown that methyl radicals can yield methane and ethylene besides dimerising to ethane.

This mechanism which we have just outlined, *viz.* (1)—(4), besides accounting for the products of the reaction, yields the correct form of the rate expression. By the usual method of stationary states we obtain :

$$-\,d[CH_3{\cdot}CHO]/dt = k_1[CH_3{\cdot}CHO][O_2] + k_1k_3[CH_3{\cdot}CHO]^2/k_4 \quad . \ . \ . \ . \quad (7)$$

If we assume that the rate of initiation is much slower than the rate of propagation we get

$$-\,d[CH_3{\cdot}CHO]/dt \sim k_1k_3[CH_3{\cdot}CHO]^2/k_4 \quad . \ . \ . \ . \ . \ . \quad (8)$$

in agreement with our experimental results.

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* The referees have pointed out that it would be better if the terminating reaction involved the destruction of the radical produced in the oxidation process. It is necessary, however, to have a terminating reaction such as the one given to obtain agreement with the experimental rate equation and to account for many of the experimental observations; and we have been unable to suggest any more reasonable reaction which is at the same time in keeping with the experimental facts.

The experimental activation energy for this reaction is, by equation (8), equal to $E_1 + E_3 - E_4$; E_3 and E_4 will be small and of the same order of magnitude though it is possible that E_4 might be slightly greater than E_3. In any event, however, practically the whole of the activation energy will be due to E_1. It is difficult to estimate E_1 with any high degree of accuracy, for there is some doubt as to the correct value for the dissociation energy of the aldehydic C–H bond, and also some uncertainty as to the correct heat of formation of the HO_2 radical. In the past, various values from 45 to 52 kcals. have been quoted for the heat of formation of HO_2; but these have been at the best inspired guesses, and there are no compelling reasons for accepting any of these values. Recently, it has been suggested (Walsh, *J.*, 1948, 331, that it might even be $\geqslant$60 kcals. Similar uncertainty prevails concerning the strength of the aldehydic C–H bond; in this case it has not always been realized that in chemical reactions one is interested in the dissociation energy of the bond and not its bond energy. Now from force-constant data (Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223) it is demonstrable that the bond energy of the aldehydic C–H bond in acetaldehyde is less than the corresponding value for formaldehyde. Skinner (*ibid.*, p. 645) has shown how the bond energies of C–H bonds vary with the length of the linkage. The length of this bond in formaldehyde being taken as 1·11 A. (Dicke and Kistiakowsky, *Physical Rev.*, 1934, **45**, 4), Skinner's data yield a value of approximately 95 kcals. for the bond energy of this linkage (see also Long and Norrish, *Proc. Roy. Soc.*, 1948, **187**, *A*, 33). Since the force constant of the aldehydic C–H bond in acetaldehyde is smaller than that in formaldehyde, we can safely assume that the bond energy will be about 92—93 kcals. Now the dissociation energy of the C–H bond in formaldehyde will be less than the bond energy by an amount equal to the reorganisation energy of the formyl radical. The latter is at present an unknown quantity but it might be as high as 20 kcals. (Walsh, Labile Molecule Discussion, Faraday Society, 1947, p. 172), *i.e.*, the dissociation energy of CH in formaldehyde may be 75 kcals. This is in agreement with the value of 78 kcals. suggested by Gorin (*J. Chem. Physics*, 1939, **7**, 256) and the value of 73—83 kcals. recently given by Gerö and Valatin (*J. Chem. Physics*, 1948, **16**, 1014).

We can find some support for these estimates in the recently determined value of 21 kcals. for the activation energy of the thermal oxidation of formaldehyde (Axford and Norrish, *Proc. Roy. Soc.*, 1947, **192**, *A*, 518). By a similar argument to that given above, it can be shown that practically the whole of this activation energy is due to the initiation reaction, and we have recently shown (*Nature*, 1948, **162**, 367) that an initiation reaction analogous to reaction (1) leads to the same rate equation as that given by Axford and Norrish. Thus, taking the heat of formation of the HO_2 radical as $\sim$52—62 kcals., we get a value of 72 $\sim$ 83 kcals. for the dissociation energy of the C–H bond in formaldehyde.

The reorganisation energy of the acetyl radical may not be so great as that of the formyl radical, but its dissociation energy may be expected to be of the same order as the C–H bond in formaldehyde, since the bond energy of the aldehydic C–H in acetaldehyde is less than the corresponding datum for formaldehyde. Using the data given by Gerö and Valatin (*loc. cit.*), it is possible to calculate the energy for the process $CH_3{\cdot}CHO = CH_3 + H(^2S) + CO(X^1\Sigma)$ as $\sim$99 kcals. Now, taking the activation energy for the reaction $CH_3{\cdot}CO = CH_3 + CO$ to be 18 kcals. (Herr and Noyes, *J. Amer. Chem. Soc.*, 1940, **62**, 2052), we calculate the dissociation energy of the aldehydic CH in acetaldehyde to be $\sim$81 kcals. Since the heat of formation of the HO_2 radical is probably $\sim$60 kcals., we get for E_1 the value $\sim$21 kcals. The experimental activation energy is $\sim$14 kcals.; there is thus a difference of $\sim$7 kcals. to be accounted for. There are two obvious explanations. The initiation may be a surface reaction, in which case the activation energy would be lowered by the heat of adsorption of the reactants. The experimental data do show an increase in the rate when the surface volume ratio is increased, but it is difficult to say whether this justifies one in assuming that the surface plays a predominant part in the initiation process. In any case, the heat of adsorption would probably be greater than 7 kcals. On the other hand, it is highly probable that the difference between E_1 and $E_{\text{obs.}}$ is simply due to $E_3 - E_4$ being approximately equal to 7 kcals., in which case the thermochemistry of the proposed initiation process is satisfactory.

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