350. *The Oxidation of Aldehydes. Part I. The Combustion Zones of Butaldehyde,* iso*Butaldehyde, Propaldehyde, Acetaldehyde, Glyoxal, and Acraldehyde.*

By D. M. Newitt, L. M. Baxt, and V. V. Kelkar.

The combustion zones of a series of saturated and unsaturated aldehydes have been mapped out over a wide range of temperatures and pressures. A comparison of the combustion diagrams indicates that the order of reactivity of the saturated aldehydes with respect to oxygen depends upon the composition of the reacting medium and upon its temperature and pressure.

The effect of a side chain is to increase the resistance of the aldehyde to oxygen attack, and the presence of a double bond alters the character of the combustion in such a way as to suggest that the processes occurring at low temperatures result in a slower building up of the critical concentration of the particular species responsible for cool flame inflammation.

The existence of three pressure limits of normal ignition have been observed in the case of the saturated aldehydes.

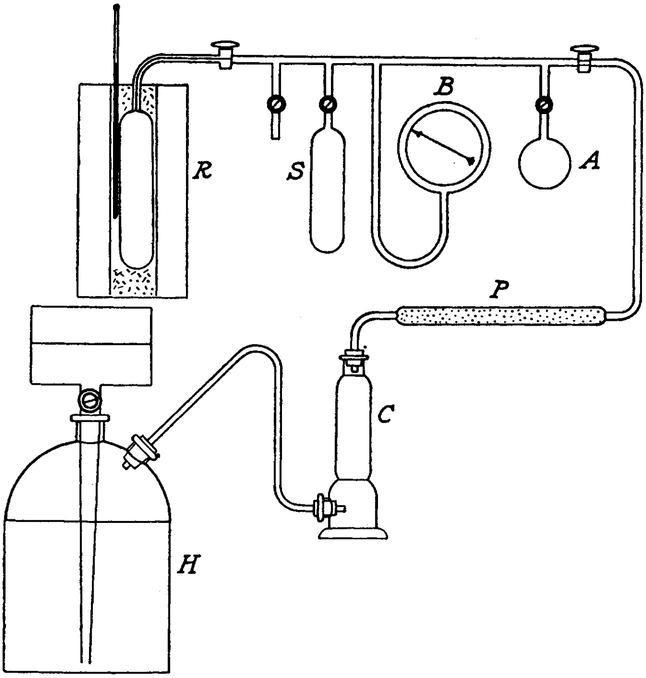
Newitt and Thornes recently showed (J., 1937, 1656) *inter alia* that some of the characteristic features of the oxidation of propane were associated with the presence, in critical concentrations, of higher aldehydes formed in the earlier stages of the combustion; and they concluded, from the results of chemical analysis, that these aldehydes reacted with oxygen in two ways, depending on the temperature and pressure of the system, yielding, on the one hand, the corresponding per-acids, and on the other, a series of lower aldehydes.

Comparatively few data upon the oxidation of the higher aldehydes in the gaseous phase are available to test this hypothesis. Pope, Dykstra, and Edgar (*J. Amer. Chem. Soc.*, 1929, **51**, 1875, 2203) examined *n*-heptaldehyde and *n*-butaldehyde in a flow system at atmospheric pressure, and suggested that in the low-temperature range, 200—335°, oxidation to lower aldehydes occurs step-wise according to the reactions:

$$\text{Main reaction: } C_nH_{2n+1}\cdot CHO + O_2 = C_{n-1}H_{2n-1}\cdot CHO + H_2O + CO$$
$$\text{Side reaction: } C_nH_{2n+1}\cdot CHO + 1{\cdot}5O_2 = C_{n-1}H_{2n-1}\cdot CHO + H_2O + CO_2$$

Bodenstein (*Sitzungsber. preuss. Akad. Wiss.*, 1931, III, 73), Hatcher, Steacie, and Howland (*Canadian J. Res.*, 1932, **7**, 1491), and Pease (*J. Amer. Chem. Soc.*, 1933, **55**, 2753) have studied the oxidation of acetaldehyde over restricted ranges of temperature, pressure, and mixture composition in static systems. They are in agreement that the combustion involves a chain mechanism and that peracetic acid is an important intermediate product, but they differ as to the precise mechanism by which chains are initiated and propagated. Hatcher, Steacie, and Rosenberg (*J. Physical Chem.*, 1934, **38**, 1189) have extended their work to include propaldehyde, and conclude that it undergoes oxidation by the same mechanism as does the lower aldehyde.

FIG. 1.



The slow oxidation of gaseous glyoxal at temperatures between 150° and 220° has been investigated by Steacie, Hatcher, and Horwood (*J. Chem. Physics*, 1935, **3**, 551), who find that the intermediate products are perglyoxylic and glyoxylic acids. No systematic work appears to have been done upon *iso*butaldehyde and acraldehyde.

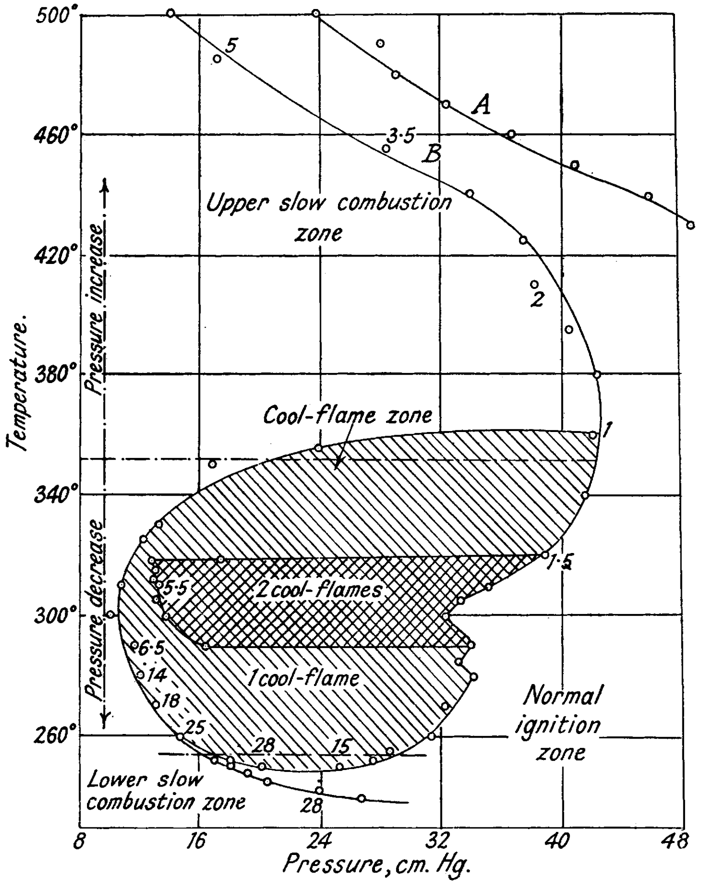
In view of the importance of aldehydes in the combustion of hydrocarbons generally, it was thought worth while to examine the oxidation of some typical members over the whole range of conditions from slow combustion to ignition, and to endeavour to link up the mechanism of their oxidation with that of the parent hydrocarbons. The results of the first part of this programme are contained in the present paper.

In their work on propane, Newitt and Thornes (*loc. cit.*) emphasised the importance of defining the experimental conditions by reference to a combustion diagram in which the slow-combustion, cool-flame, and true ignition zones are accurately demarcated; and the same considerations apply to aldehydes. No data applicable to experiments in the pressure range 10—76 cm. Hg are, however, available. The work of Prettre (*Bull. Soc. chim.*, 1932, **51**, 1152) is confined to one pressure, and that of Kane, Chamberlain, and Townend (J., 1937, 436) covers a range of some 5 atm. It was, therefore, necessary at the outset to construct the requisite reference diagrams for mixtures of such composition that all three combustion zones would fall within a pressure range of *ca.* 1 atm., and that the ignitions at all temperatures would be comparatively mild in character. Mixtures containing 9—20% of aldehyde and 91—80% of ($2N_2 + O_2$) were found to be suitable, the proportions being varied according to the number of carbon atoms contained in the aldehyde.

EXPERIMENTAL.

The apparatus employed is shown in Fig. 1. Redistilled aldehyde * was dried over anhydrous sodium sulphate and stored in the blackened bulb *A*. The oxygen–nitrogen mixture was made in the gas-holder *H* and passed into the apparatus through a tower *C* containing calcium chloride and a tube *P* containing freshly distilled phosphoric anhydride. The combustible mixture was made in the vessel *S* to such a pressure that, when it was placed in communication with the reaction vessel *R*, the resultant pressure was that required for the experiment. Mixing was effected by means of glass beads contained in *S*.

FIG. 2.



Combustion zones of propaldehyde.

The cylindrical reaction vessel was made of transparent silica and had a capacity of *ca.* 500 c.c. It was enclosed in an electric furnace the temperature of which was read by means of a mercury thermometer calibrated at frequent intervals against a standard thermometer. As mercury vapour was found to exert a marked catalytic effect both upon the rate of polymerisation of the aldehyde and upon its combustion, precautions were taken to exclude it from the

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* Glyoxal was prepared from the solid polymer by heating with phosphoric acid (Harries and Temme, *Ber.*, 1907, **40**, 165).

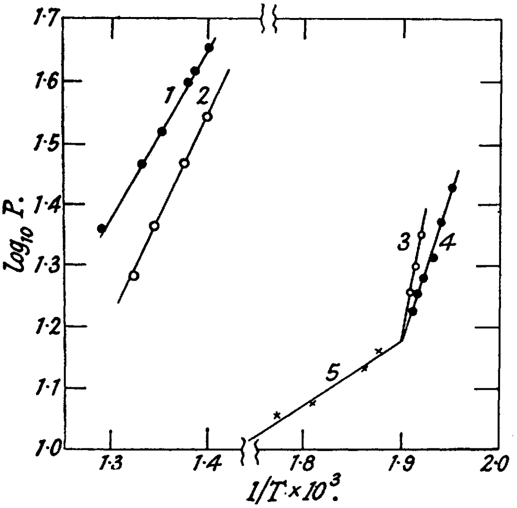
system. In place of the mercury manometer usually employed in such experiments, a 12-inch Bourdon gauge, calibrated in degrees, was used.

In order to maintain the surface of the reaction vessel in a uniform state of activity relative to the reaction, a strict ritual was observed during each series of experiments. The surface was first " normalised " by carrying out a number of experiments at short intervals until the rate of reaction became substantially constant. Subsequently, after each experiment, the bulb was washed out with air and evacuated at the reaction temperature for 15 minutes. In this way satisfactory reproducibility was obtained.

The cool-flame and the normal-ignition temperatures were measured by introducing a mixture of constant composition into the vessel at a series of progressively increasing pressures until two pressures were found, differing by not more than 5 mm., at the lower of which ignition did not take place and at the upper of which it did.

It should be borne in mind that the absolute values of the ignition temperatures and pressures depend to some extent upon the experimental method and upon the nature of the surface of the reaction vessel. The general character of the ignition temperature–pressure curves, however, is not materially altered by surface conditions provided the surface is " normalised " as described above (Townend, Cohen, and Mandlekar, *Proc. Roy. Soc.*, 1934, *A*, **146**, 113).

FIG. 3.



1 = *Upper ignition (mercury).*
2 = *Upper ignition (mercury-free).*
3 = *Low pressure ignition (upper curve).*
4 = *Low pressure ignition (lower curve).*
5 = *Cool flame.*

A Comparison of the Combustion Diagrams.—(1) *Propaldehyde.* Since our original intention was to confine the work to those aldehydes produced by the combustion of propane, propaldehyde was the first to be investigated. In the preliminary experiments, a mercury manometer being used to record pressures, the upper slow combustion and ignition zones for a 12% propaldehyde–88% ($2N_2 + O_2$) mixture were mapped out. The boundary curve is shown in Fig. 2, Curve *A*. On attempting to continue the curve to lower temperatures, unexpectedly erratic results were obtained, the pressure required for ignition at any one temperature sometimes varying by more than 50% in successive experiments. Eventually it was discovered that mercury vapour was influencing the results,* and on replacing the manometer by a Bourdon gauge, Curve *B* was obtained in which the reproducibility was satisfactory throughout the whole range of temperatures and pressures. The horizontal distance between the two curves gives a qualitative measure of the inhibiting influence of mercury vapour on the oxidation.

In general, the diagram is similar to that of propane, although the aldehyde is always the more reactive. The phenomenon of multi-cool flames is again observed, but their number never exceeds three. An interesting feature of the diagram is the low-pressure ignition peninsula between 240° and 255°. It will be observed that in this region a series of isotherms may be drawn representing temperatures at which there are three pressure limits of normal ignition with an intervening zone in which cool-flame combustion alone takes place. It will be shown later that this phenomenon is characteristic of the higher saturated aldehydes although it tends to disappear on ascending the series.

The critical pressures at which ignition occurs should, according to Semenov (" Chemical Kinetics and Chain Reactions," 1935), be related to the absolute temperature by the expression $\log_{10}P = C/T + D$, in which C and D are constants, the former depending upon the relative efficiencies of surface and gas molecules in breaking the chains, and the latter upon the dimensions of the reaction vessel and the composition of the mixture. This relation may be applied to Curve *A*, the upper part of Curve *B*, and the boundary curves of the low-pressure ignition peninsula and cool-flame zone.

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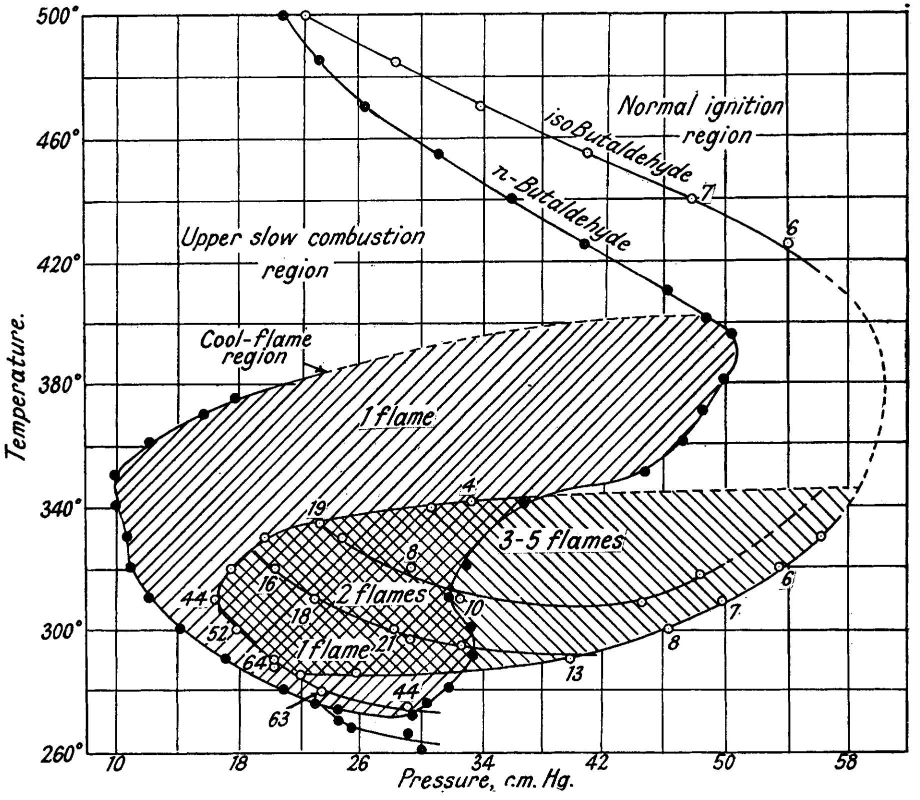
* The carbon, hydrogen, and oxygen balances from the analyses showed that rapid polymerisation of the aldehyde was taking place with very little oxidation. Acetaldehyde exhibited the same phenomenon.

On plotting $\log_{10}P$ against $1/T$ it will be seen from Fig. 3 that satisfactory straight lines are obtained. The values of the constants C and D for the five curves are as follows :

	C.	D.
Curve A	2680	− 2·1
Curve B : (1) Upper slow-combustion boundary curve	3230	− 3·0
(2) Cool-flame boundary curve	1080	− 0·86
(3) Inner low-pressure ignition curve	6670	−11·40
(4) Outer low-pressure ignition curve	4160	− 6·70

The variation of the constant D for the cool-flame curve and the adjacent normal ignition curves is an indication that different mechanisms are concerned.

FIG. 4.



Combustion zones of n-*butaldehyde and* iso*butaldehyde.*

The numerals adjacent to the boundary curves in Fig. 2 give the time-lags in seconds preceding ignition. They are shorter than the corresponding lags of the parent hydrocarbon but vary in much the same way with temperature and pressure. It is also noteworthy that, whereas at about 350° slow combustion takes place with no measurable change in pressure, yet above this temperature there is an increase and below a diminution in pressure.

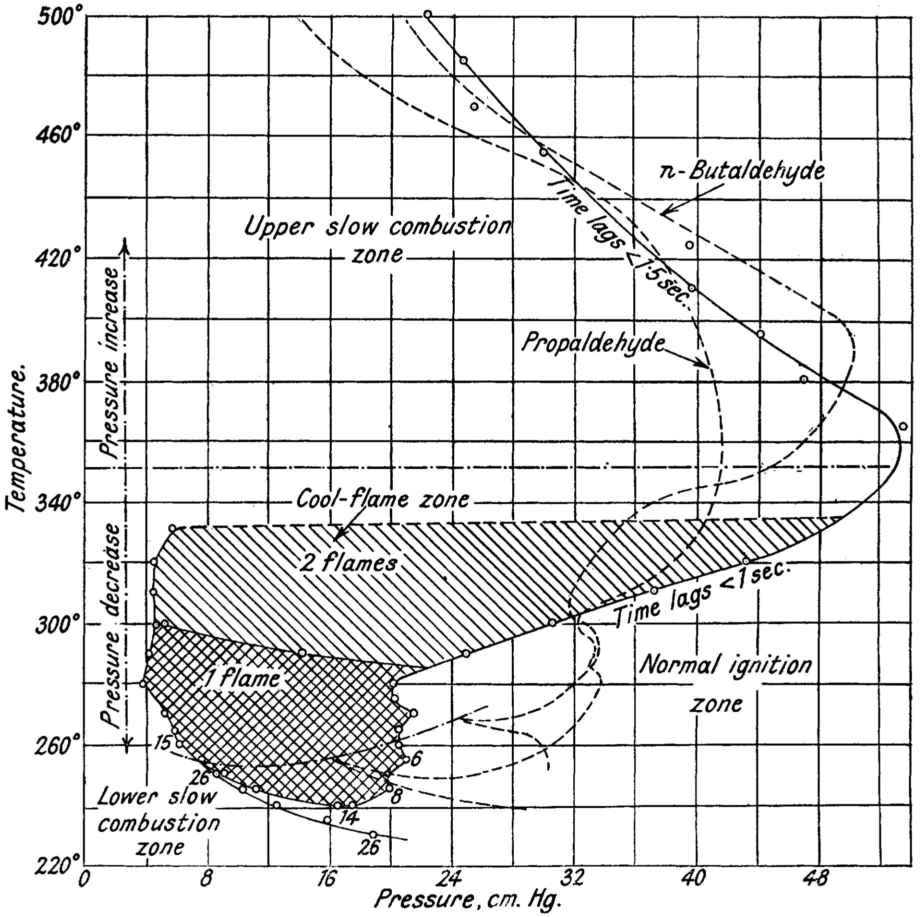
(2) n-*Butaldehyde and* iso*butaldehyde*. The influence of a side chain upon the reactivity of aldehydes is shown by a comparison of the combustion diagrams of *n*- and *iso*-butaldehyde (Fig. 4). In each case the mixture employed contained 9·42% of aldehyde in ($2N_2 + O_2$).

Attention may be directed to the following points : (*a*) At all pressures the normal aldehyde is the more reactive; (*b*) whereas multi-cool flames are not observed with the *n*-aldehyde, as many as five successive flames may be formed by the *iso*-aldehyde; (*c*) the low-pressure ignition peninsula noted with propaldehyde extends over about 1° in the *n*-aldehyde and is present only in a rudimentary form in the *iso*-aldehyde; and (*d*) reaction in the slow-combustion zones is accompanied by an increase in pressure in both cases.

(3) *Acetaldehyde.* The combustion diagram of an 18·8% acetaldehyde in ($2N_2 + O_2$) mixture is shown in Fig. 5. It resembles in all essential respects that of propaldehyde. Above 350° the slow combustion occurring in the region to the left of the ignition curve is accompanied by an increase of pressure, whilst below 350° there is at first a rapid decrease of pressure, followed after some time by a slow increase. In the cool-flame zone two successive flames were always formed above 295° and a single cool flame below this temperature.

For purposes of comparison the ignition temperature–pressure curves for propaldehyde and *n*-butaldehyde are shown on the same diagram. It will be seen at once that the order of reactivity of the three aldehydes depends upon the temperature and pressure. For instance, between 300° and 420° and above 450° propaldehyde is more reactive than acetaldehyde. The order of reactivity between 300° and 345° is *n*-butaldehyde, propaldehyde, acetaldehyde, whilst in the lower slow-combustion zone the order is reversed, acetaldehyde being the most reactive.

FIG. 5.



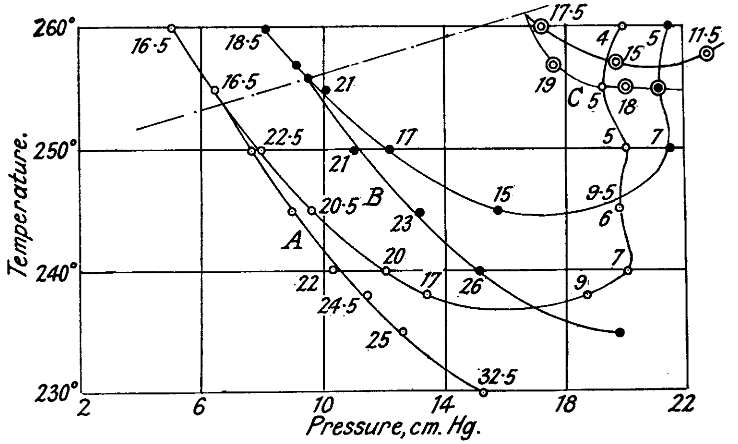
Combustion diagram of acetaldehyde.

The low-pressure ignition peninsula is well defined for acetaldehyde and extends over some 12°. A few experiments were carried out to ascertain the effect of the concentration of the combustible on the form and extent of this region. In Fig. 6, Curves *A*, *B*, and *C* refer to mixtures containing 23·0, 14·6, and 7·3% of aldehyde, respectively. As the concentration increases, the boundary of the peninsula widens and the apex moves in the direction of lower pressure and temperature. As with propaldehyde, a linear relation is found to hold between $\log_{10}P$ and $1/T$ for the boundary curves in this region.

The occurrence of three pressure limits of explosion is not uncommon, and several examples have been studied in detail (cf. Neumann and Egorow, *Physikal. Z. Sowietunion*, 1932, **1**, 536;

Neumann and Serbinoff, *J. Physical Chem. Russ.*, **1933**, **4**, 41; Foord and Norrish, *Proc. Roy. Soc.*, **1935**, *A*, **152**, 196). The phenomenon, as exhibited by hydrogen, methane, and ethane, has well-defined characteristics which receive adequate explanation in terms of a combination of chain and thermal mechanisms. Thus, the dependence of the lower limit on the dimensions of the reaction vessel and the nature of its surface, and its independence of temperature, suggest that deactivation at the walls is a determining factor; the intermediate limit, on the other hand, is independent of the dimensions and surface of the vessel, is displaced towards higher pressures by increase of temperature, and is probably controlled by deactivation in the gas phase. The upper limit is associated with a purely thermal explosion due to a departure from isothermal conditions as the rate of reaction accelerates.

FIG. 6.



A = 23·0% $CH_3{\cdot}CHO$, 77·0% ($2N_2 + O_2$).
B = 14·6% $CH_3{\cdot}CHO$, 85·4% ($2N_2 + O_2$).
C = 7·3% $CH_3{\cdot}CHO$, 92·7% ($2N_2 + O_2$).

The limits for aldehydes are essentially of a different kind from the above, for, whereas the lower limit of a $2H_2 + O_2$ mixture at 550° is at a pressure of about 8 mm., that for a 23% aldehyde in ($2N_2 + O_2$) mixture is some 12 times greater. Deactivation at the walls cannot, therefore, in this instance, be regarded as a likely determining factor. It is also noteworthy that both the lower and the intermediate limits move in the direction of lower pressures, and approach one another, with rise of temperature, until eventually they meet and there is a unique temperature at which two limits only exist. The upper limit shows no marked variation with temperature.

The induction periods of the lower and upper limits decrease and those of the intermediate limit increase with rise of temperature. Finally, the region between the intermediate and upper limits is one in which cool-flame inflammation occurs, probably due to a reaction of the degenerate branching chain type. The chemical changes occurring in the neighbourhood of the three limits afford some indication of the mechanisms concerned and are discussed in the succeeding paper.

(4) *Glyoxal.* Glyoxal occurs as an intermediate in the slow oxidation of acetylene and is also, by virtue of its structure, of importance in connexion with the mechanism of aldehyde oxidation generally.

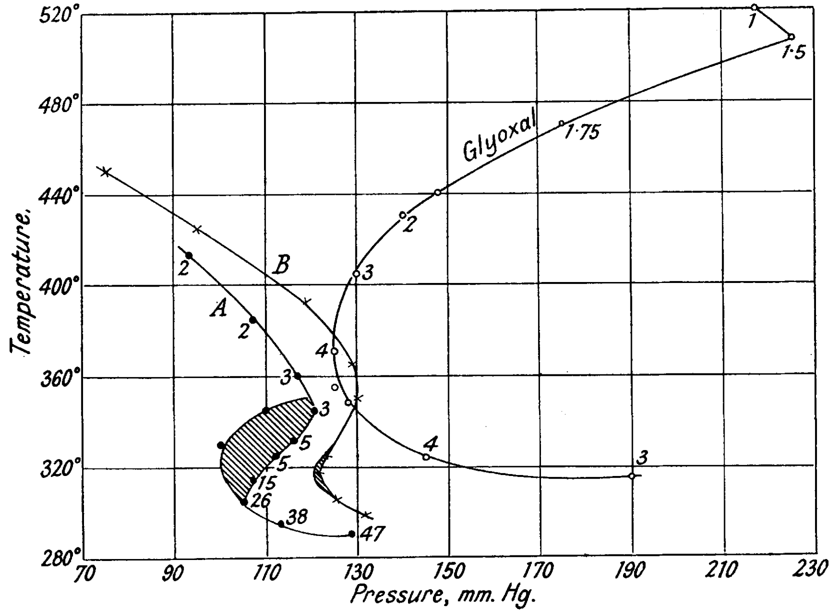
The combustion diagram of a $(CHO)_2 + O_2 + N_2$ mixture (Fig. 7) exhibits some interesting features when compared with those of the other aldehydes just considered. In particular, although there is a well-defined low-pressure ignition system, cool flames are not formed and the pressure minimum of ignition occurs at a much higher temperature, as will be seen from the following figures:

Aldehyde.	Pressure minimum of ignition, cm. Hg.	Corresponding ignition temp.
Acetaldehyde	9·0	250°
Propaldehyde	16·0	268
n-Butaldehyde	24·0	272
*iso*Butaldehyde	22·0	286
Glyoxal	12·5	370

On the other hand, it differs from that of formaldehyde in which there is no low-pressure system (Kane, Chamberlain, and Townend, *loc. cit.*).

(5) *Acraldehyde.* The combustion diagrams of two acraldehyde–oxygen–nitrogen mixtures are included in Fig. 7, and illustrate the influence of a double bond in modifying the characteristics of the combustion. In both cases the low-pressure ignition region is less clearly defined than with the saturated aldehydes and the minima occur at higher temperatures, namely, at 305° for the $CH_2{:}CH{\cdot}CHO + O_2 + N_2$ mixture (Curve *A*) and at 319° for the $CH_2{:}CH{\cdot}CHO + 2O_2 + N_2$ mixture (Curve *B*). The cool-flame zones are also of smaller extent, and the flames themselves are comparatively weak and are accompanied by only a feeble pressure pulse. In this respect the behaviour of acraldehyde resembles that of the higher olefins (cf. propylene; Kane and Townend, *Proc. Roy. Soc.*, 1937, *A*, **160**, 174).

FIG. 7.



Combustion zones of glyoxal and acraldehyde.

Conclusions.—A comparison of the various combustion diagrams indicates that the order of reactivity of the saturated aldehydes with respect to oxygen depends upon the temperature, pressure, and composition of the reacting medium; and in studying the course and mechanism of their oxidation it is, therefore, necessary to specify the experimental conditions by reference to the corresponding diagram for the mixture concerned. It will be observed that all the previous work upon the oxidation of aldehydes, with the exception of that of Pope, Dykstra, and Edgar, and of Townend and his collaborators, has been confined to a restricted region at the low-temperature boundary of the diagrams.

In order to interpret the results obtained it is necessary first to supplement them by an identification of the products formed at various stages of the oxidation and by a systematic study of its kinetics. The analytical results are described in the succeeding paper.

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