350. *The Oxidation of Propane. Part III. The Kinetics of the Oxidation.*

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The conditions under which the reaction of an equimolecular propane–oxygen medium has a negative temperature coefficient have been investigated, and the coefficients for the surface and homogeneous reactions measured separately.

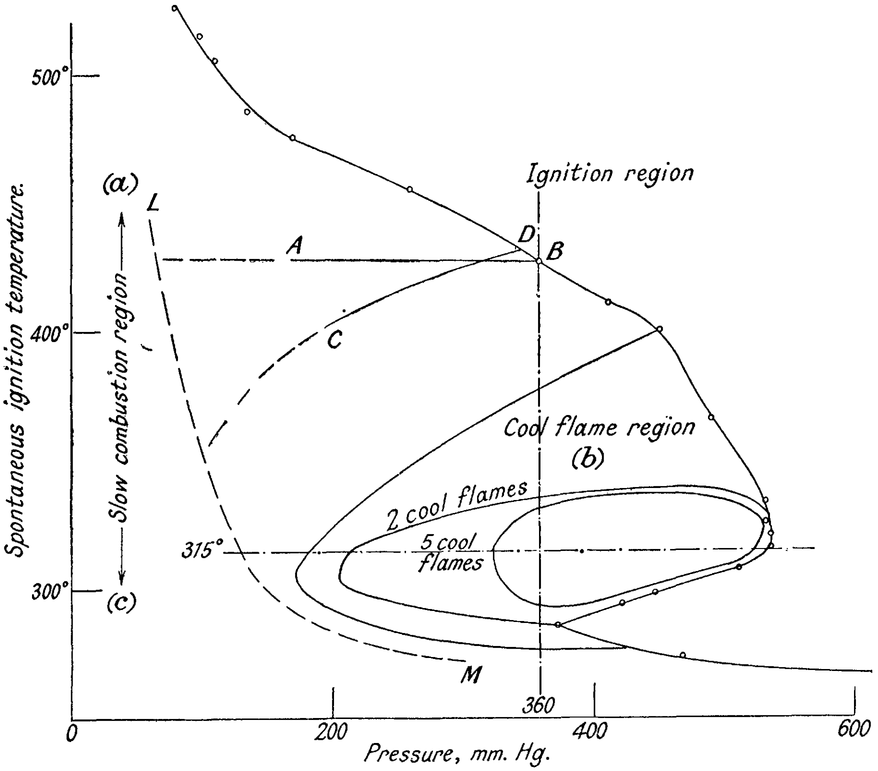
The influences of vessel diameter and of diluents on the rate of reaction are shown to be such as would result from the operation of a chain mechanism. The analytical and kinetic results as a whole suggest that the intermediate stages exerting a controlling influence on the course and rate of the combustion are: (1) an initiating process which almost certainly starts as a surface reaction and gives rise to critical concentrations of a higher aldehyde, (2) a series of homogeneous reactions by which the higher aldehyde is reduced stepwise to formaldehyde, and (3) a reaction occurring simul-

taneously with (2) and resulting in the aldehyde (or some intermediate product of its further oxidation) undergoing thermal decomposition.

THE results of numerous investigations covering a wide range of experimental conditions have shown that the oxidation of the paraffin hydrocarbons is characterised by an induction period during which a surface reaction takes place and small concentrations of certain intermediate products are built up, followed by a gas-phase reaction which has usually, though not invariably, the characteristics of a chain reaction. The homogeneous reaction of the lower members of the series, methane and ethane, has a positive temperature coefficient, and its progress may be followed by measuring the change of pressure with time in a closed system or by the rate of oxygen consumption.

FIG. 1.

Combustion regions of a $C_3H_8 + O_2$ *medium.*



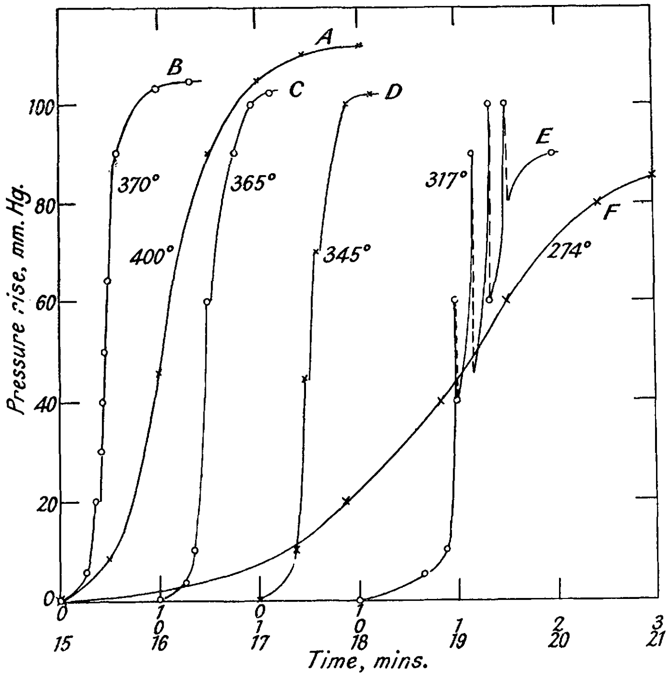
On ascending the series, the phenomena associated with the homogeneous reaction become more complex and, as shown in Part I, it is necessary to distinguish four types of reaction which may conveniently be defined by reference to an ignition temperature–pressure diagram such as that shown in Fig. 1. This refers to an equimolecular propane–oxygen medium reacting in a closed silica vessel; to the right of the full-line curve is a region in which spontaneous ignition always occurs after a comparatively short induction period, and to the left are three regions in which (*a*) high-temperature slow reactions, (*b*) cool-flame reactions, and (*c*) low-temperature slow reactions, severally, take place. The cool-flame region may also be further sub-divided by a system of closed curves defining the conditions under which single and multiple cool flames are observed.

Slow combustion in the regions (*a*), (*b*), and (*c*) is characterised by certain features associated with the changes in the reactivity of the medium with temperature. For instance, if the pressure–time curves for a series of experiments along the 360-mm. isobaric lines are compared, as in Fig. 2, it will be seen that in (*a*), curve *A*, there is an induction period of about 0·25 sec., followed by a rapid reaction during which the pressure rises uniformly to a maximum; in (*b*) the four curves *B*, *C*, *D*, and *E* show the incidence of cool flames, the number of flames increasing as the temperature is lowered; and in (*c*), curve *F*, the reaction is again normal, there being an induction period of 15 mins. followed by a slow pressure rise extending over a further 7 mins.

In curve *E*, the formation of four separate cool flames at intervals of approximately 10 secs. is clearly indicated; each flame is accompanied by a rapid rise, and its extinction is followed by an equally rapid fall in pressure, the extent of the changes being such as might well result from the variations in temperature associated with the passage of the flame. At the moment of formation of the first flame only about 10% of the oxygen present is consumed, the ratio oxygen : propane taking part in the reaction up to this point being 1·4.

FIG. 2.

Pressure–time curves of a $C_3H_8 + O_2$ *medium.*



At 345° (curve *D*) two cool flames are formed with no definite interval between them, and visual observation shows that the second flame starts before the first is quite extinguished. At 356° and 370° (curves *C* and *B*) only one flame is produced, which continues to burn until reaction is nearly complete.

It was shown in Part I that the initiation of a cool flame synchronises with the attainment of a critical concentration of higher aldehydes in the medium, the further oxidation of the aldehydes by reactions resulting in their degradation to formaldehyde being responsible for the flame propagation. The concentration of higher aldehydes at any moment is determined by their respective rates of formation and further oxidation; in the low-temperature, slow-combustion region (*c*), for example, both rates are slow and of the same order of magnitude, so that high concentrations are never reached, whilst at a somewhat higher temperature, in region (*b*), there is evidence that the rate of formation increases rather more rapidly than that of further oxidation, and critical concentrations are readily attained. The intensity of each cool flame will depend upon the concentration of the aldehydes relative to the critical concentration, and the occurrence of multiple cool flames will only be possible in a restricted zone in which a balance exists between the rates of formation and oxidation of the aldehydes. In this connection the analytical results (Part I, Table III) show that even after the passage of a cool flame a relatively large amount of higher aldehydes still remains in the medium.

The mechanism of the oxidation of the higher aldehydes has not yet been satisfactorily elucidated, and until further experimental data are available it is not possible to identify the individual steps by which they are transformed into lower members of the series. Reference may be made, however, to experiments by Pope, Dykstra, and Edgar (*J. Amer. Chem. Soc.*, 1929, **51**, 1875, 2203) upon the oxidation of *n*-octane, in which there is evidence that octaldehyde is oxidised directly to heptaldehyde with the liberation of carbon monoxide or dioxide and water :

$$CH_3{\cdot}[CH_2]_6{\cdot}CHO + O_2 = CH_3{\cdot}[CH_2]_5{\cdot}CHO + H_2O + CO$$

and

$$CH_3{\cdot}[CH_2]_6{\cdot}CHO + 1\tfrac{1}{2}O_2 = CH_3{\cdot}[CH_2]_5{\cdot}CHO + H_2O + CO_2$$

Our experiments, on the other hand, indicate that an aldehyde peroxide and/or per-acid is an important stabilised intermediate product, and that during the passage of a cool flame two processes are operative, the one leading to the ultimate formation of formaldehyde and the other to simpler products as the result of the thermal decomposition of one or more of the intermediates taking part in the main reaction. If the oxidation of the higher aldehyde proceeds by a chain mechanism, the latter process would cause chain breaking and would satisfactorily account for an upper limit of cool flame propagation.

Evidence for a Chain Mechanism.—Egerton (*Nature*, 1928, **121**, July 7, Suppl.), Norrish (*Proc. Roy. Soc.*, *A*, 1935, **150**, 36), Ubbelohde (*ibid.*, *A*, **152**, 354), and von Elbe and Lewis (*J. Amer. Chem. Soc.*, 1937, **59**, 976) have recently summarised the evidence in favour of a chain theory of hydrocarbon combustion, and have suggested definite mechanisms by which the available kinetics and analytical data for the simpler hydrocarbons may be interpreted; the corresponding data for the higher members, however, are still incomplete, and until more is known as to the nature and identity of the intermediate products of their oxidation no direct application of any of the proposed mechanisms is possible. In the case of propane, however, the general characteristics of the slow combustion as already described, and the additional kinetic data given below, are such as would result from the operation of branching or degenerate branching chains.

The Relative Reactivities of Propane–Oxygen Media.—It will be recalled that the most reactive methane– or ethane–oxygen medium is one containing the hydrocarbon and oxygen in the ratio 2 : 1, and any excess of either reactant above these proportions gives rise to a marked retardation in both the slow and the explosive combustion (cf. Bone and Hill, *Proc. Roy. Soc.*, *A*, 1930, **129**, 434).

With the higher hydrocarbons, a satisfactory comparison can only be obtained in the high-temperature, slow-combustion region, and in such circumstances the 1 : 1 hydrocarbon–oxygen medium is found to be the most reactive. For instance, it will be seen from the pressure–time curves in Fig. 3, which refer to the reaction at 360 mm. and 408° of a series of propane–oxygen mixtures, and the inset curve showing the relation between reaction velocity ($\Delta P/\Delta t$) and hydrocarbon concentration, that the velocity of this mixture is considerably greater than that of either the 2 : 1 or the 1 : 2 mixture; a similar result is obtained when the rate of oxygen consumption is plotted against the hydrocarbon concentration. Corresponding observations have also been recorded for pentane–oxygen mixtures by Pidgeon and Egerton (J., 1932, 661).

The Influence of Diluents and of the Dimensions of the Reaction Vessel.—In a chain process in which the chains originate and/or terminate at the walls of the reaction vessel, the rate of reaction is found to depend *inter alia* upon the dimensions of the vessel and the composition of the medium, and the effect of increasing the diameter of the vessel or of adding an inert diluent will result in an increase. Since the spontaneous ignition temperature of a combustible medium is the temperature at which the reaction attains a certain critical velocity, the influence of the above factors may readily be determined by a comparison of the ignition temperature–pressure data.

The curves *A* and *B* in Fig. 4 show graphically the relation between the spontaneous ignition temperature and total pressure for the two mixtures $C_3H_8 + O_2$ and $C_3H_8 + O_2$

+ N_2, respectively, and the broken curve *B′* the data for the nitrogen-diluted mixture plotted in the basis of the partial pressure of ($C_3H_8 + O_2$); the numerals placed opposite

FIG. 3.

Influence of hydrocarbon concentration on the rate of reaction of propane–oxygen media.

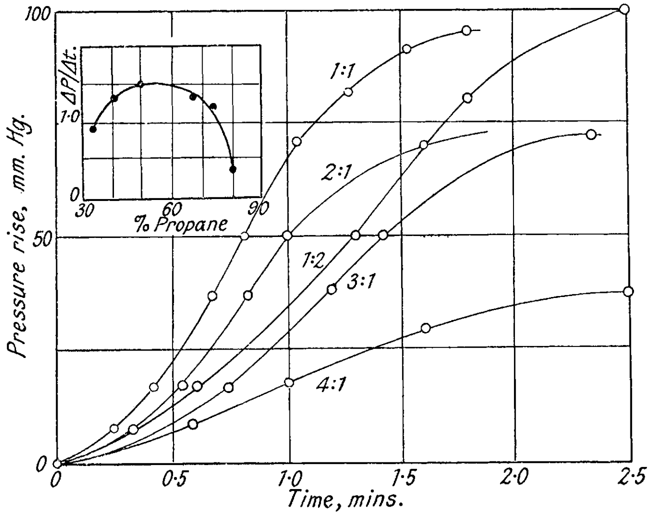
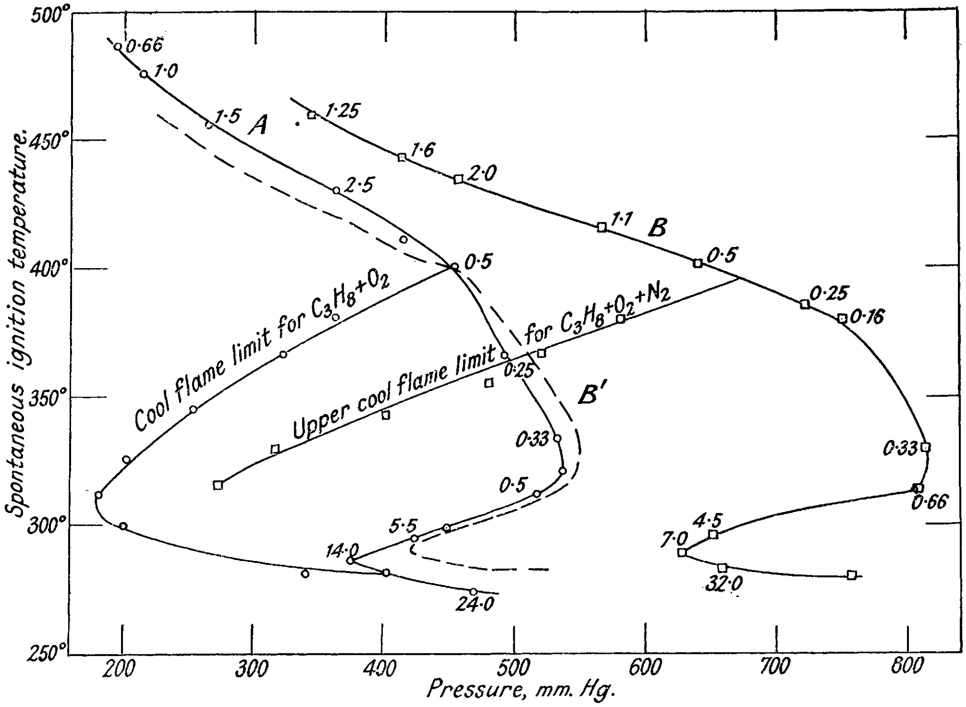


FIG. 4.

Influence of nitrogen dilution on the ignition temperature of a $C_3H_8 + O_2$ *medium.*



the experimental points in the curves give the induction periods in minutes before ignition occurs.

By comparing curves *A* and *B′*, it will be seen that addition of nitrogen raises the lower limit of inflammation by about 15°, increases the critical transition pressure by about 20 mm., and raises the lower cool-flame limit without appreciably altering the upper limits. In the cool-flame region between 295° and 395° it retards, and above this region it accelerates, the reaction. From the standpoint of a chain mechanism these results suggest either a relative change in the extent to which chain-breaking occurs on the walls and in the gas phase on passing from the cool-flame to the slow-combustion region, or an influence of the diluent on chains initiated at the walls.

That chain-breaking occurs predominantly at the walls may be inferred from a comparison of the critical ignition pressures of an equimolecular propane–oxygen mixture reacting in vessels of different diameters. The data in Table I for three glass vessels of diameters 2·5, 3·7, and 4·8 cm., severally, show, for example, that both in the cool-flame and the slow combustion region, the pressure p at which ignition occurs is a function of the diameter of the vessel d, the product pd^n being a constant and n having a value of 0·46; and this relation has been shown, on theoretical grounds, to hold for all chain processes in which the chains are broken principally at the walls (Semenoff, " Chemical Kinetics and Chain Reactions," Oxford, 1935). Furthermore, the lower temperature limit of inflammation, which is substantially independent of pressure over a wide range, narrows as the diameter is reduced, as follows :

TABLE I.

Ignition pressure of a $C_3H_8 + O_2$ medium in vessels of different diameters.

Diameter of vessel, cm.		4·8	3·7	2·5
	Ignition temp.	Critical pressure, mm.		
Slow combustion zone	450°	590	670	800
	425	650	745	865
	400	670	790	910
Cool flame zone	375	635	735	860
	350	615	695	820
	325	625	705	825
	300	550	590	735

Diameter of vessel, cm.	4·8	3·7	2·5
Lower temperature limit of inflammation	270°	280°	285°

Attention may also be directed to the marked sensitivity of the oxidation reaction to " wall " conditions. It is found that both the duration of induction and the subsequent rate of reaction are influenced by the previous history of the vessel; and each time the vessel is cleaned it is necessary, in order to obtain reproducible results, to " sensitise " its surface by carrying out an ignition experiment in the high-temperature zone.

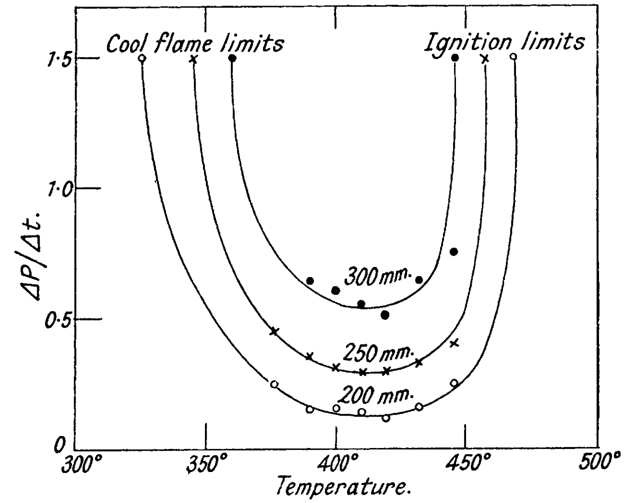
The Negative Temperature Coefficient.—It will be clear from an inspection of the ignition curve in Fig. 1 that, if true ignition be related to reaction velocity according to the thermal view, the variation of ignition temperature with pressure must be associated with a negative temperature coefficient of the reaction in the cool-flame and high-temperature slow-combustion regions, and that in the latter region there will be limiting conditions for which the coefficient will have a zero value.

Pease (*J. Amer. Chem. Soc.*, 1929, **51**, 1839) first directed attention to the occurrence of negative values in the oxidation of a $C_3H_8 + O_2 + 2N_2$ medium in a flow system at atmospheric pressure and 350—400°, and similar isolated observations have been made for pentane, heptane, and octane (Aivazov and Neumann, *Acta Physicochim.*, 1936, **4**, 575; Beatty and Edgar, *J. Amer. Chem. Soc.*, 1934, **56**, 112). The flow method, however, is not well adapted to the measurement of the temperature coefficients of reactions having comparatively long induction periods, nor does it enable a distinction to be drawn between the coefficients of the surface and the homogeneous reaction and the influence of pressure upon them. A static method similar to that described in Part I, on the other hand, allows the two reactions to be examined separately, and a wide range of conditions in respect of temperature and pressure to be employed.

The region of particular interest is that in which slow combustion takes place above the upper limit of cool-flame propagation (see Fig. 1). Experiment shows that on progressively increasing the reaction temperature from the upper cool flame limit, the pressure being maintained constant, the rate of reaction at first diminishes, passes through a minimum at which the temperature coefficient is zero, and then increases until finally ignition takes place. The relation between pressure increase and time for reactions in this region (Curve *A*, Fig. 2) indicates that, after a short induction period, oxidation occurs uniformly, and from the slope of the pressure–time curves the rate of reaction ($\Delta P/\Delta t$) can be measured. The curves in Fig. 5 show graphically the variations in reaction rate with temperature for an equimolecular propane–oxygen mixture at 200, 250, and 300 mm. pressure, severally; they all terminate at low temperatures in cool-flame ignition, and at high temperatures in true ignition, their minima corresponding with a temperature of 420°. It is thus possible to indicate on Fig. 1 by means of a straight line *AB* the conditions under which the slow reaction has a zero coefficient, and a region between *AB* and the upper limit of cool-flame propagation in which the coefficient is negative. In the cool-flame region itself, reaction proceeds *per saltum* with alternate accelerations and retardations of velocity, and the influence of temperature can only be compared over restricted phases of the reaction.

FIG. 5.

Influence of temperature on the rate of reaction of a $C_3H_8 + O_2$ *medium.*



The velocity of the surface reaction can be measured approximately by the duration of the induction period. With an equimolecular propane–oxygen medium at 360 mm., for example, reaction is first detectable at about 280°. At 285° the induction period is 5 mins. and on progressive increase of temperature it diminishes until at 365° it is about 5 secs., or comparable in magnitude with the time taken in filling the reaction vessel. With further increase of temperature, the induction period passes through a minimum and thereafter increases steadily until the ignition point is reached, whereat it has a value of *ca.* 30 secs. At or immediately above the ignition temperature the coefficient again changes sign and the induction period diminishes with further rise.

The relation between induction period and temperature for the above medium at 360, 300, 250, and 200 mm. is shown by the curves in Fig. 6; it will be seen that in the experiments at 360 and 300 mm. the minima occur at about the upper cool-flame limits.

The temperature at which the coefficient for the surface reaction becomes zero increases with pressure as shown by the line *CD* (Fig. 1), and the two loci for the homogeneous and for the gas phase reactions meet at the true ignition curve. The low-pressure extremities of these two lines would probably terminate on the curve *LM*, which marks the limits of temperature and pressure at which no discernible reaction takes place after 2·5 hours;

the triangular area enclosed by the three curves would then be one in which the temperature coefficients of the two reactions have opposite signs.

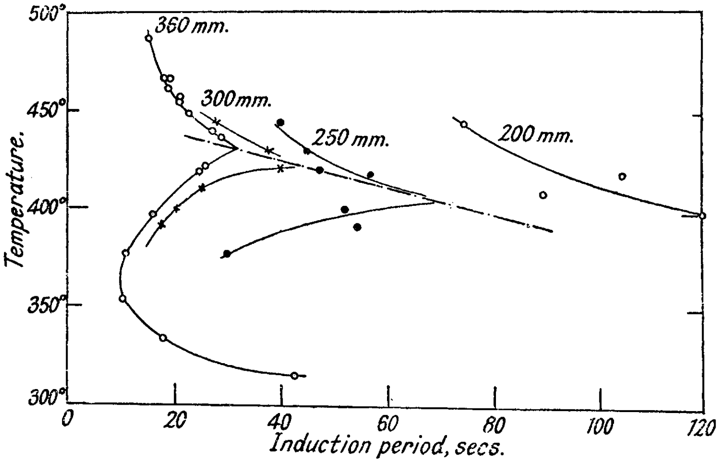


FIG. 6.

Variations of the induction periods of a C_3H_8 + O_2 medium with temperature.

On traversing an isothermal line in the cool-flame region, the induction period is found to diminish as the pressure is progressively raised. The data at 315° are as follows :

Pressure, mm.	515	437	382	321	194
Induction period, mins.	0·5	0·5	1·5	2·83	14·0

DISCUSSION.

The occurrence of a negative temperature coefficient in a complex process nearly always means that the integrated effect of two or more dependent reactions is being observed; and in the present instance the analytical results are in conformity with this view. It was shown in Part I that the high-temperature, slow-combustion reaction of propane is always accompanied by intense luminescence and by the formation of comparatively high concentrations of higher aldehydes and of peroxidic substances; the latter reach a maximum at a somewhat later stage than do the former, and there is evidence that they result from the further oxidation of the aldehydes. There is, indeed, little doubt but that the kinetics of the process depends to a large extent upon the mechanism of this oxidation, and further work upon it is now in progress.

The analytical and kinetic results as a whole suggest that the factors determining the main course of the oxidation of the higher hydrocarbons are by no means as complex as is generally supposed, the number of intermediate steps which may be assumed to exert a controlling influence on the course and rate of the combustion being strictly limited.

The principal facts can be accounted for by the operation of three processes leading to the formation of stabilised intermediate products which may be recognised by chemical analysis. These are : (1) an initiation process which almost certainly starts as a surface reaction and gives rise to the formation of critical concentrations of an aldehyde having the same number of carbon atoms as the parent hydrocarbon, (2) a series of homogeneous reactions by which the higher aldehyde is reduced stepwise to formaldehyde, and (3) a reaction occurring simtaneously with (2) and resulting in the aldehyde, or some intermediate product of its further oxidation, undergoing thermal decomposition; if, as seems probable, chain mechanisms are involved in (1) and (2), this reaction would, by terminating the chains, account for the observed limits of cool-flame propagation and for the negative temperature coefficient. Furthermore, any of the recently suggested chain mechanisms based upon the formation and interaction of radicals would, on certain reasonable assumptions, give rise to the above sequence of changes.

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