85. *The Oxidation of Pentane and Other Hydrocarbons. Part I.*

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THE discovery of " anti-knock " substances, and the subsequent search for their mode of action, has resulted in the suggestion that the combustion of a hydrocarbon is catalysed by some active oxygenated compound or " moloxide," the formation of which is the initial step in the mechanism of oxidation (Egerton and Gates, Aer. Res. Comm., No. 1079, 1926; Callendar, King, and Mardles, No. 1062, 1926). This suggestion received strength during the rapid growth of the conception of chain reactions and its application to hydrocarbon combustion (Hinshelwood and Thompson, *Proc. Roy. Soc.*, 1928, **118**, 170; Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, **125**, 277).

It was pointed out (*Nature*, 1928, **122**, 204) that "peroxidation" was not necessarily inconsistent with Bone's "hydroxylation" theory, for, once initiated, the combustion might proceed by a variety of paths; this was shown to be probable by Hinshelwood and Thompson (*loc. cit.*) in the case of ethylene combustion: several investigators (Mardles, J., 1928, 873; Rideal and Brunner, *ibid.*, pp. 1126, 2824) have obtained evidence for the peroxidation as an initial step in the process of oxidation of a saturated hydrocarbon. On the other hand, Bone, in a study of slow combustion of ethane, upholds the views that no such peroxide is formed, and that the oxidation proceeds by stages of hydroxylation, an alcohol being the first step. He allows that at the aldehyde stage there may be formed a certain amount of peroxide by a secondary process. Pope, Dykstra, and Edgar (*J. Amer. Chem. Soc.*, 1929, **51**, 1875) consider that reaction with oxygen immediately gives an aldehyde and water, whereas Berl, Heise, and Winnacker (*Z. physikal. Chem.*, 1928, **139**, 453) and Lewis (J., 1927, 1555) suggest dehydrogenation, and production of an unsaturated molecule is necessarily the first stage.

The object of the present communication—the extension of some earlier work on the oxidation of acetaldehyde, etc.—is not so much to provide evidence for one or other of these processes, as to collect further information on the behaviour of some of the higher hydrocarbons on oxidation, before attempting to explain what must inevitably be intricate. Since the commencement of the work, much has been published on combustion of unsaturated hydrocarbons, etc. (*e.g.*, Lenher, *J. Amer. Chem. Soc.*, 1931, **53**, 3737; Lenher and Kistiakowsky, *ibid.*, 1930, **52**, 3785; Bodenstein, *Z. physikal. Chem.*, 1931, *B*, **12**, 151), which, from the kinetics of the processes considered, indicates a direct addition of the oxygen to the activated fuel molecule as an initial step, but in the case of saturated hydrocarbons the assimilation of the oxygen molecule is not so easily understood, so it is of importance to obtain definite information of the behaviour of such compounds.

One of the authors (A. C. E.) (*Nature*, Supplement, July 7, 1928), by inference from the general behaviour of inhibited combustion; made certain assertions: (1) the slow hydrocarbon combustion was a chain reaction, (2) the products of later stages of combustion influenced the initial stages, and (3) the inhibitor is oxidised before it is effective. The present work was carried out in order to prove these points.

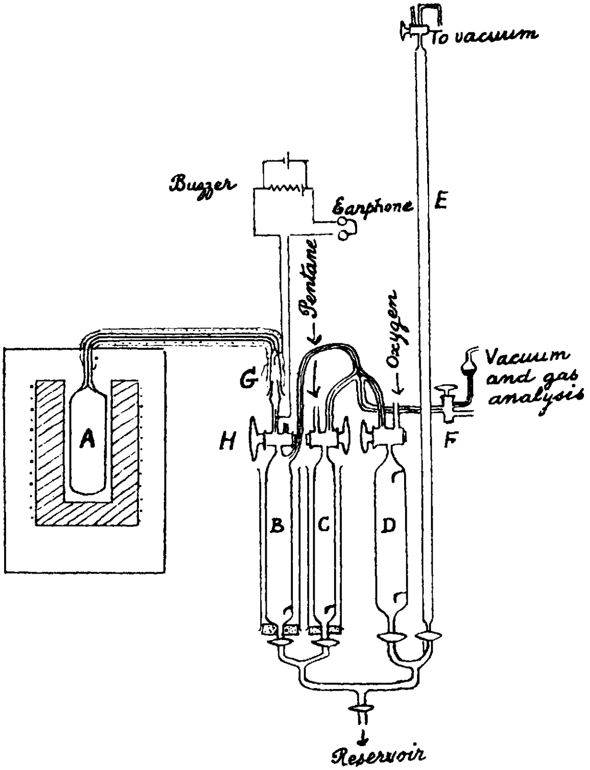
The combustion of pentane has been investigated statically, the effect of pressure and concentration on (1) the temperature at which combustion commences to become rapid and (2) the velocity of reaction being studied. Similar investigations have been carried out on hexane, amylene, and valeraldehyde, and the influence of one combustible on another has been determined; these results will be found in Part II (following paper), together with a note on the inhibitory action of lead tetraethyl. It is found in all cases that the general characteristics of a chain reaction are manifested. An induction period, during which no change in pressure is noticed, precedes the attainment of the true rate of reaction, and many factors, such as wall surface, inert gas, etc., affect the length of the period. No attempt to discuss the kinetics of the combustion in detail has been made, as the number of possible reactions is very great in the case of the higher hydrocarbons. The method employed in these experiments was the "static" or constant-volume bulb method, the mixture of hydrocarbon vapour and oxygen being heated at a known temperature, and the change of pressure observed [compare Bone and Townend, "Flame and Combustion," p. 558; Hinshelwood; Mardles; Rideal and Brunner (*locc. cit.*)].

EXPERIMENTAL.

Apparatus.—The apparatus is illustrated in Fig. 1. While fulfilling the general requirements of this type of apparatus, it offers certain advantages: condensation of reactants or their products as liquids is prevented, and the method of introduction of the reactants is simple, allowing a considerable range of fuel pressure to be utilised. *C* and *D* are calibrated constant-volume burettes, in which the volumes of fuel and oxygen are measured by noting the pressure on the manometer *E*. The fuel burette is maintained at a higher temperature than the outside atmosphere to prevent liquid condensation of fuel therein. The interconnecting tubing is also electrically heated to a slightly higher temperature. The hydrocarbon and oxygen are passed from their respective burettes into the mixing chamber *B*, also suitably heated. By opening the tap *H*, the mixture is forced into the reaction bulb *A* by the mercury rising in the mixing chamber, which, by suitable manipulation of the taps at the base, becomes the left arm of the manometer *E* by which the pressure measurements are then made.

The capillary connecting the manometer and the reaction bulb is electrically heated to a temperature well above the b. p. of any of the reactants or their products of combustion (generally 75—120°). Although invisible owing to this jacketing, the left arm of the manometer has to be brought to a constant position for each reading. A platinum point sealed into the base near the end of the capillary enables the setting to be accurately made, for the mercury, on touching this point, completes a circuit in which a very small interrupted current is detected by means of high-resistance telephones (4000 ohms). In the case of higher-boiling compounds, such as hexane and valeraldehyde, it was difficult to prevent some condensation in the measuring burette when mercury was run in to displace the gas. This difficulty was overcome by cooling the reaction bulb in carbon dioxide snow and thus distilling the fuel into it. This technique, however, is not available for the examination of reaction velocity, as it is necessary to introduce the mixture into

Fig. 1.



the bulb without delay at the temperature in question. In this case it is necessary to employ a lower partial pressure of fuel.

At the conclusion of an experiment the mercury is withdrawn from the interconnecting tubing through the tap *F* connecting the apparatus to the evacuating system. The gases are passed through a cooled trap, and the dry gaseous products delivered to a burette. With the latter is incorporated the gas-analysis apparatus. The whole apparatus is very thoroughly evacuated with a two-stage mercury-vapour pump backed by an oil pump.

By means of the ground joint *G* the reaction system may be removed for cleaning. This joint also provides a means of transition from the apparatus of soft glass to a bulb of Pyrex glass or silica. During the reaction the left arm of the manometer stands well above this joint, forming a closed system.

Between each experiment, the bulb and interconnecting capillary were removed and washed with boiling chromic acid, followed by boiling distilled water and sometimes acetone. (For pentane, the tube could be cleaned by heating with air, followed by evacuation, the process being repeated several times. The experiments subsequent to this treatment showed no difference from those after the tube had been washed as described above; in fact, they were rather more uniform. Hexane and some of the other compounds deposited a tarry residue, which could only be dislodged by strong acid.)

The furnace consisted of a block of aluminium wound with nichrome wire, insulated from the block by a thin sheet of mica, and well lagged. Temperatures were measured with a mercury thermometer, checked against N.P.L. standards, with careful attention to stem correction. Thermometers were placed both in the central chamber and in holes bored in the block. A mercury-in-glass thermo-regulator maintained the temperature constant to 0·05°.

Preparation of Reactants.—The oxygen was prepared by heating potassium permanganate, the gas being passed over soda-lime and stored over phosphoric oxide.

The source of the *n*-pentane was a petroleum distillate. It was shaken with fuming sulphuric acid to remove any unsaturated compounds, washed with water, and dried with metallic sodium. It was then further purified by crystallisation, followed by fractionation. The portion of b. p. 34·5—35·0°/755 mm. was employed.

Results.—As pointed out by Bone in 1902, reaction takes place with measurable velocity over a considerable range of temperatures well below the ordinary ignition point (*e.g.*, ethane and oxygen at 1·75 atmos. showed signs of incipient reaction at 265°). The lower limit of this region is not sharply defined, and may be strongly influenced by a number of factors, such as surface, hence it is unsuitable as a point on which to base comparisons of the ease of initiation of reaction. For such purposes it is convenient to employ what may be called the "reacting temperature." If a gaseous mixture of a hydrocargon and oxygen is heated in a closed tube provided with a manometer, as temperature increases at a constant rate, a certain point will be reached at which the pressure increases sharply above the normal gas expansion curve, indicating reaction with the production of an increased number of molecules. This point, although dependent upon a number of arbitrary factors, is remarkably reproducible in a given apparatus, and forms a useful means of recognising the pure hydrocarbon and studying the effect of various factors on the ease of initiation of combustion. Mardles, Lewis, and Brunner and Rideal (*locc. cit.*) have already shown that there is a temperature at which the combustion more or less suddenly begins to become rapid, although not explosively so. It has also been shown that the combustion is preceded by an induction period.

Using *n*-pentane, we have investigated (*a*) the influence of various factors on the " reacting temperature " ; (*b*) the velocity of reaction.

(*a*) A 50% mixture at 760 mm. total pressure if heated at a rate of 0·6° per min. from an initial temperature of 210° (there is no reaction at this temperature during 90 min.) gives a reacting temperature of 245—246°, reproducible to ± 1°. The point of inflexion is not sharp in most cases, but indicates that preliminary reaction exists which accelerates to the constant rate indicated by the steep part of the curve. The reaction ends fairly abruptly, and the normal gas expansion curve * is resumed at higher pressure.

Effect of pressure. This is indicated in Table I and Fig. 2. Over a considerable range, alteration in pressure does not greatly affect the position of the reacting temperature, although the amount of reaction is changed as shown by the percentage pressure increase. Near the lower limits of pressure, the reacting temperature is appreciably raised. The effect of total pressure is, however, fairly uniformly manifested within the range investigated.

TABLE I.

Effect of total pressure on a 1 : 1 *mixture of pentane–oxygen.*

Pressure, mm.	1040	760	550	400	340
Reacting temp.	240°	245°	247°	248°	257°
Pressure increase, % ...	—	10·2	8·6	6·7	4·7

Concentration of reactants. The effect of varying the concentration

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* This is dependent on the composition of the gas and on its behaviour on expansion.

is illustrated in Table II. At a given pressure, a 1 : 1 mixture reacts most readily, although it does not exhibit the greatest amount of reaction as calculated from pressure increase.

FIG. 2.

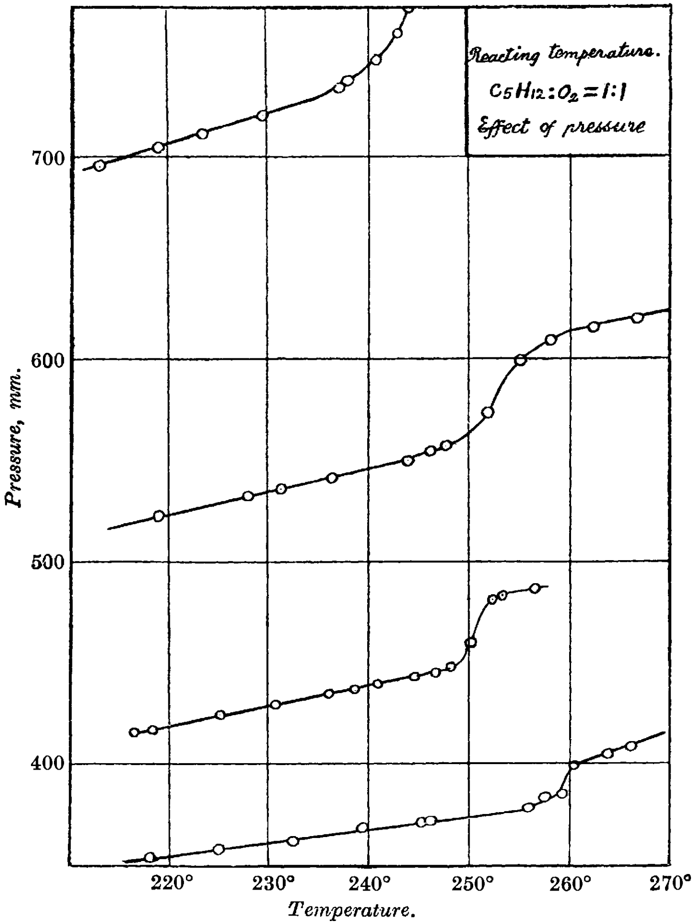


TABLE II.

Effect of concentration of reactants on reacting temperature.

Pressure, mm.	Conc. (C_5H_{12} : O_2).	Reacting temp.	Pressure increase, %.
555	1 : 6	260°	5·9
590	1 : 3	251	16·1
540	1 : 1	247	8·6
590	2 : 1	250	6·5

The amounts of fuel which are required for slow combustion are greatly in excess of the theoretical. This illustrates the difference between the initiation of a reaction and its propagation after it has been started. A theoretical mixture of pentane and oxygen (1 : 8) would have a very high reaction temperature, and would probably react explosively. This fact is again illustrated in Table II in which the 1 : 3 mixture shows the greatest pressure increase.

It is noteworthy that the 1 : 1 mixture reacts more readily than a higher concentration of fuel, for Bone and Hill (*Proc. Roy. Soc.*, 1930, **129**, 434) found the 2 : 1 mixture to be the most reactive in the case of ethane, and considered it as evidence in favour of the initial formation of two molecules of a primary alcohol by the collision of two fuel molecules with an oxygen molecule, though, indeed, the reason may equally well be ascribed to the nature of the chain reaction. It is probable that somewhat different processes take place in the case of higher hydrocarbons.

The amount of reaction (as indicated by pressure increase, which, owing to the complicated nature of the products, is not necessarily a true measure of the extent of reaction) is affected both by concentration and by pressure. With the 1 : 1 mixture, the percentage increase in pressure is somewhat less than that calculated on the basis of the reaction $7C_5H_{12} + 7O_2 \longrightarrow 3CO_2 + 2CO + 6H_2O + 6C_5H_{12}$, it being assumed that the excess fuel does not react and appears on the other side of the equation. In this case the increase should be 21·5%, with which may be compared the practical values ranging from 6% to 10% according to the pressure. The reaction, however, does not follow this simple course : products such as aldehydes are formed, and stabilised during the course of the reaction.

Effect of surface. The nature and extent of the surface affect the reacting temperature, as shown below and in Fig 3.

Effect of type of surface on reacting temperature of 1 : 1 mixture of C_5H_{12} *and* O_2.

	Pressure, mm.	Reacting temp.	Pressure increase, %.
Soda glass	775	246°	10·2
Pyrex glass	805	242	10·0
Silica	820	237	10·0

Effect of increased surface.

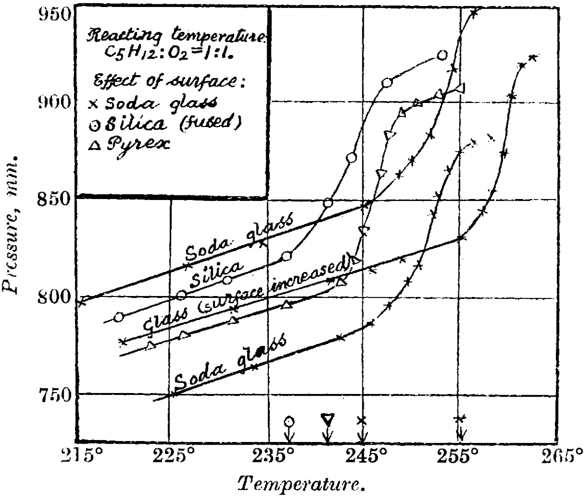
Soda glass bulb : surface 131 sq. cm.			
	800	245	10·5
Packed with tubes 1 cm. diameter, total surface 462 sq. cm.			
	810	255	9·8

Hence it appears that in the case of pentane the chains are propagated in the gas, and are broken on the walls. The different effect of various surfaces represents their " chain-breaking " power.

Glass is the most chemically active surface of those under discussion, hence the temperature of reaction is highest in a glass vessel. Increase in glass surface exerts a powerful inhibitory effect on the reaction, and may even prevent a reaction which would otherwise have taken place (see later).

If an inert gas is added, the reacting temperature is appreciably lowered. The addition of 300 mm. of nitrogen to a 1 : 1 mixture of pentane–oxygen at 700 mm. total pressure, lowers this temperature from 245° to 241°. This agrees with observation on the other hydrocarbons (Thompson and Hinshelwood, *loc. cit.*). The chains are fairly long, and normally terminate on the surface of the reaction vessel, so that when the number of collisions between molecules of the reacting gas and the walls is reduced by the addition of inert molecules, the whole reaction is accelerated.

FIG. 3.

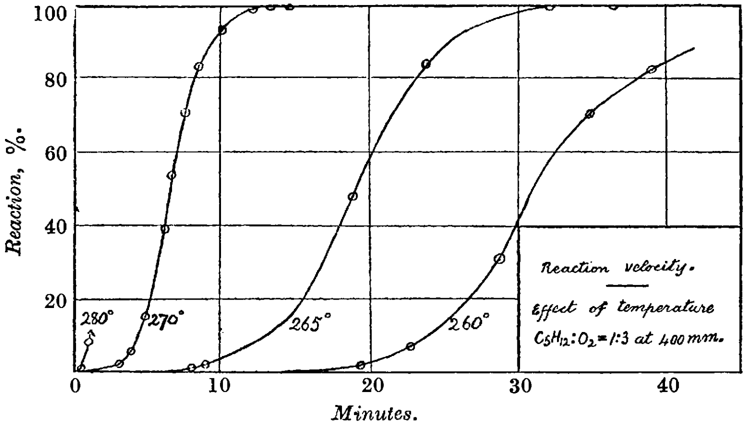


It appears that the effect of walls did not alter the course of the reaction, for in all cases the amount of pressure increase was the same. The rate of reaction in the case of the packed bulb was more rapid, as would be expected from the fact that a higher temperature must be reached before the reaction is initiated.

Rate of heating. It is apparent from the curves that reaction begins prior to the point which is considered as the reacting temperature. Hence the rate of heating will influence the magnitude of this quantity. Rapid heating will carry the mixture to a higher temperature than slow heating before reaction occurs, as it does not give time for the preliminary steps which are necessary for reaction at these temperatures. These differences are not as large as might have been expected, and it is a simple matter to control this variable (compare Lewis, J., 1930, 58).

The reaction mixture was usually heated at a rate of 0·6° per min., starting from an initial temperature of 210°. The reacting temperature of a 1 : 1 pentane–oxygen mixture at 760 mm. under these conditions is 254°. Very much slower heating lowers it to 243°, and when the gas is run into the reaction vessel at 240°, and the furnace heated as rapidly as possible, a temperature of 250° is attained. This explains the wide differences in values for the reacting temperature which are found between the static and dynamic (or flow) methods of oxidation. In the latter case, the gas as a whole is held for a shorter space of time in that region of temperature in which the active centres can accumulate. Hence a higher temperature must be reached to compensate for the lack of time.

FIG. 4.



(*b*) *Velocity of Reaction.*—If a mixture of oxygen and pentane is admitted to the bulb at some suitable temperature, reaction takes place after the lapse of an induction period during which little change in pressure is noticed. In the case of a 1 : 4 pentane : oxygen mixture at a total pressure of 400 mm., the measurable reaction extends from approximately 230°, at which it is barely perceptible, to 280°, at which explosion (rapid reaction with flame) occurs. Carbon is deposited in the tube in a fine furry condition, an occurrence which does not take place during the normal measurable reaction. The kinetics of oxidation in the region between these two limits have been examined to show the effect of temperature, pressure, surface, etc. In view of the interest attached to the initial stages of reaction, experiments at relatively low temperatures with higher pressures and concentration of fuel have been carried out at 220°.

By plotting time against pressure increase (as a percentage of the final pressure increase), sigmoid curves are produced (Fig. 4) which are characteristic of gaseous oxidation of hydrocarbons. After the induction period, the rate of reaction is fairly constant over a range of approximately 40—80% of reaction on the above basis. In the tables which follow, this value represents the reaction rate after the induction period has been completed, and before the reaction begins to slacken owing to consumption of the reactants or retardation by end products.

A Pyrex bulb of approximately 90-c.c. capacity was used as the reaction vessel.

Effect of temperature. The variation of reaction velocity with temperature is indicated by the following data :

O_2, mm.	C_5H_{12}, mm.	Temp.	$t_{0.5}$, mins.	$t_{0.8} - t_{.04}$, mins.
310	110	280°	1·0	(Explosion)
314	111	270	6·7	2·0
311	84	265	19·5	5·0
311	92	260	32·0	7·2

An appreciable induction period is always observed even when the ensuing reaction takes place explosively (see Fig. 4).

In general a linear relation connects the logarithm of $t_{0.5}$ (the time to half value) with the reciprocal of the absolute temperature. The heats of activation corresponding to these curves are about 50,000 cals., but not enough is known of the nature of the reaction to justify any definite conclusions as to the length of the chains.

Effect of pressure (*order of reaction*). The numerical values showing the effect of pressure on the reaction velocity are given below : the effect is most marked in the induction period.

$C_5H_{12} : O_2 = 1 : 1$, at 266°.

Pressure, mm.	$t_{0.5}$, mins.	$t_{0.8} - t_{0.4}$, mins.
202	(No reaction)	—
299	13·0	1·3
423	4·7	0·9
504	3·0	0·1

When log P is plotted against log $t_{0.5}$ an approximately straight line is produced, corresponding to an order of reaction between 2 and 3.

Concentration of reactants and reaction velocity. The effect of alteration in concentration of fuel and of oxygen is as shown :

Variation in conc. of O_2 (at 265°).

O_2, mm.	C_5H_{12}, mm.	$t_{0.5}$, mins.	$t_{0.8} - t_{0.4}$, mins.
203	90	29·0	5·1
311	84	19·5	6·6
407	90	8·0	3·7

Variation in conc. of C_5H_{12}.

O_2, mm.	C_5H_{12}, mm.	$t_{0.5}$, mins.	$t_{0.8} - t_{0.4}$, mins.
203	220	4·6	1·3
203	156	8·3	1·0
203	90	29·2	5·1

Alteration in fuel concentration entails greater change in the reaction velocity than a corresponding change in oxygen concentration. These facts are in accord with the general properties of chain reactions. It appears that the reaction is most readily propagated when the initial activated complex collides with a second fuel molecule.

Addition of inert gas. Addition of 200 mm. of nitrogen to a 1 : 3 pentane : oxygen mixture at 400 mm. total pressure reduces the time for half reaction from 19 to 12 mins. This effect is noticed largely during the induction period, in agreement with the suggestion that the inert gas keeps the active centres which propagate chains of reactions from becoming deactivated on the walls, thus indicating that the chains may not be short.

(*b'*) *Reaction Velocity at Low Temperature.*—By increasing the total pressure and the fuel concentration, it is possible to obtain reaction at lower temperatures. Slow reaction was obtained as low as 220°, with a long induction period. The results in this region were usually erratic, probably because the great time required by the reaction allowed abnormal factors to exert their effect. It was, for example, impossible to detect any definite acceleration by the addition of inert gas.

Effect of temperature. Experiments at various temperatures with a 1 : 1 pentane–oxygen mixture at 780 mm. total pressure are given below :

Temp.	$t_{0.5}$, mins.	$t_{0.8} - t_{0.4}$, mins.	Press. increase, %.
220·6°	147·0	27	7·2
233·2	80·5	19	7·5
231·0	68·0	19	7·5
239·0	48·5	13	8·5

The erratic nature of the results is evident. When $1/T$ is plotted against the logarithm of $t_{0.5}$ a straight line is not produced : the curve flattens at low temperatures, denoting an abnormally low temperature coefficient. In view of the shape of the curve, denoting as it does a complex process, it is not possible to attach any special meaning to values of activation energy calculated therefrom.

Effect of pressure. The effect of pressure on reaction below the normal region of reaction is shown by the following data for a 1 : 1 mixture at 231° :

Pressure, mm.	$t_{0.5}$, mins.	$t_{0.8} - t_{0.4}$, mins.	Pressure increase, %.
421	173	35	7·5
766	68	18·5	8·3
1115	57	15·0	7·3

The induction period is again most sensitive to alteration in pressure ; otherwise the reaction proceeds in a similar way, the increase in pressure is the same, and gas analysis indicates a similar reaction.

Effect of surface. Increase in wall surface exerts a powerful effect on the reaction at low temperatures. When a soda-glass surface is increased 3·4-fold, a 1 : 1 mixture at 231° and 800 mm. total pressure fails to react after 2 hours' heating. The time to half reaction in this case would normally be about 1 hour. In spite of the marked effect of packing the bulb, no definite effect of inert gas could be detected. In some cases a definite acceleration was noticed, but in as many others no change occurred. Hence it seems that in this region, while surface exerts its customary effect of breaking chains, in some way the inert gas fails to prevent this chain breaking. It appears that chance circumstances often govern the course of events during the very long induction period. On many occasions, reactions, which later proceeded with identical velocity, showed quite a different length of induction period. These differences were relatively large, in some cases over 10 minutes.

Analysis of Gaseous Products of Combustion.—The analyses here considered were in all cases performed on the dry gaseous products obtained by passing the combustion products through a trap cooled in carbon dioxide snow. The apparatus used included a special absorption pipette, in which the gas was washed with a fountain of fresh absorbent (Egerton and Pidgeon, *J. Sci. Inst.*, 1931, **8**, 7). It would be difficult to effect a complete analysis of all the products of combustion of pentane, and would entail a long investigation. The analyses were only intended as a check on the general behaviour of the combustion, and a few notes on them are added.

The average composition of the end products of a number of oxidations of a 1 : 1 mixture at 760 mm. total pressure, which were heated from 210° to 260° in the manner described previously, was CO_2, 27·0; CO, 30·0; O_2, 5·0; residue, 38·0%. Although all the oxygen is not consumed, a combustible residue remains. Its amount depends on the concentration of oxygen in the original mixture, being small if a large excess of oxygen is used. This is illustrated in the following table. All the gas could be pumped from the apparatus, and collected for analysis, hence these results show the actual amounts of gas added to, and removed from, the apparatus after the experiment, with the volumes corrected to *N.T.P.*

Gas added, c.c.		Gas collected, c.c.			
O_2.	C_5H_{12}.	CO_2.	O_2.	CO.	Residue.
21·0	24·0	3·8	1·0	3·7	4·3
11·5	23·6	3·2	1·1	3·1	7·2
28·2	9·1	6·4	4·4	5·1	3·2

In the first two cases the amounts of carbon oxides produced are substantially the same, but where there is a deficiency of oxygen a large amount of residue is produced; *i.e.*, the initial stages of the reaction depend mainly on the fuel concentration, and variation in oxygen concentration does not affect so much the initial reaction as the subsequent steps.

This is further seen by a consideration of oxygen consumption. The carbon oxides indicate the fate of part of the oxygen. If it is assumed that for every carbon atom which appears as an oxide 1 mol. of water is formed (disposing of the organic group CH_2), at least a comparative means of tracing the oxygen is offered. If this is done in the case of the 1 : 1 mixture listed in the above table, 42% of the added oxygen may be accounted for, the remainder having gone to form complex compounds such as aldehydes and acids, which are removed by condensation in the trap. In the second case ($C_5H_{12} : O_2 = 2 : 1$), 77% of the oxygen is accounted for, almost the same amounts of carbon oxides being formed. On the other hand, in the last case ($C_5H_{12} : O_2 = 1 : 3$) 64% can be accounted for. Hence the 1 : 1 mixture seems to form the largest amount of aldehydes, etc., in the final products.

In the case of reaction at low temperatures, as described in the previous section, larger proportions of condensable oxygenated compounds are formed, the amount being considerably reduced by increase of oxygen concentration; for instance, at 231° a 1 : 1 mixture accounts for only 33% of the original oxygen, while a 1 : 3 ($C_5H_{12} : O_2$) mixture shows 50%.

Induction period. Many analyses were performed on the products of reaction removed from the mixture at various stages of the induction period in the case of a reaction performed at low temperature. The results were :

$C_5H_{12} : O_2 = 1 : 1$; 800 mm. total pressure.

Final pressure increase, %.	CO_2, %.	O_2, %.	CO, %.	Residue, %.
100·0	44·0	6·2	25·3	42·5
3·0	0·7	92·6	3·0	3·3
4·1	1·0	85·5	5·5	8·3
11·0	7·4	64·6	3·7	22·5

The induction period is considered to be complete after 10% of the pressure increase has taken place; during this time it is apparent that oxygen is being absorbed, but at the same time considerable amounts of carbon monoxide and residue are formed, accompanied by a small amount of carbon dioxide. During the induction period, the fall in pressure which would be expected owing to absorption of oxygen is balanced by the attendant decomposition of some of the active complex to carbon oxides.

It is of interest to compare the values of oxygen consumption during the induction period as found by other investigators. Rideal and Brunner (*loc. cit.*) found that 30% of his oxygen had reacted before the rapid reaction would set in. Fort and Hinshelwood (*Proc. Roy. Soc.*, 1930, **127**, 218), in the case of benzene, found that after 4% reaction, 11% of the oxygen had been utilised. Bone and Hill (*loc. cit.*) found no chemical change whatsoever with ethane till the end of the induction period. It seems clear that there is a difference in the behaviour of the higher hydrocarbons and the lower members; and further experiments are being made.

Conclusion.

The kinetics of the oxidation of pentane point to the existence of reaction chains. An induction period exists, during which the active centres are accumulating. The chains are initiated in the gas, and broken at the wall of the containing vessel; thus, addition of an inert gas produces acceleration. Reaction takes place most easily in the case of a 1 : 1 mixture, although when once initiated, more vigorous reaction is produced by higher concentrations of oxygen. Both the effect of pentane concentration on the velocity of reaction and the results of gas analysis show that the early stages of the reaction are dependent on the initial concentration of pentane, and not on that of oxygen. It has been shown that reaction will take place at lower temperatures, but in this region the results are more erratic.

The general evidence from these experiments is that the initial step in the oxidation of pentane is the formation of an oxygenated complex by collision between a molecule of fuel and one of oxygen, reaction being propagated when this complex collides with a second molecule of fuel. The momentary absorption of an oxygen molecule into the hydrocarbon molecule would lead to breakdown into an aldehyde. Reaction occurs mainly at the surface by a different mechanism until temperatures in the neighbourhood of the "reacting temperature" are reached. Although active centres from which chains of reaction start out must be formed during the induction period, the surface is exerting its effect in stopping the chains. The surface therefore probably plays a double rôle. The exact nature of these initial steps, however, has yet to be explained.

Summary.

(i) The temperature at which reaction proceeds rapidly in pentane–oxygen mixtures increases as the pressure decreases, and is lowest for a mixture of equal concentration of pentane and oxygen. The temperature is lower in a silica vessel than in one of glass, and is raised with increase in surface. The addition of nitrogen lowers this reacting temperature.

(ii) The effects of temperature, pressure, and concentration on the

reaction velocity were determined. The reaction velocity is affected more by change of fuel concentration than by that of oxygen.

(iii) The effects of temperature, pressure, surface, and diluents on the period of reaction preceding rapid reaction were investigated : they were somewhat irregular, as might be expected from the nature of the period of induction.

(iv) The oxidation has the general characteristics of a chain reaction.

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