

## 86. *The Oxidation of Pentane and Other Hydrocarbons. Part II.*

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IN continuation of Part I (preceding paper), experiments have been made (a) on the oxidation of hexane, amylene, valeraldehyde, *iso*-pentane, *iso*amyl alcohol, and (b) on the effect of these substances on the oxidation of pentane. A note is added on the action of lead tetraethyl as an inhibitor of the oxidation of pentane. The main object of these experiments was (i) to determine the behaviour on oxidation of various substances which might be formed in the early stages of the oxidation of pentane, so as to provide information about the latter process, and (ii) to discover whether the presence of a small quantity of a mixture already reacting could initiate the oxidation of pentane at a lower temperature than that at which it would otherwise react.

The experimental arrangements were similar to those described in Part I.

(a) *Hexane*.—The hexane examined was a petroleum distillate, b. p. 67—68°/741 mm. It was freed from unsaturated compounds and distilled from metallic sodium.

*Reacting temperature*. At 620 mm. total pressure, a 1 : 1 mixture reacts at 223° in a Pyrex bulb, and at 224° in a glass bulb. These values are lower than that, *viz.*, 232°, obtained by Brunner and Rideal under somewhat similar conditions.

*Reaction velocity*. The kinetics of the oxidation of hexane in the gaseous state have been examined in a similar manner to that described for pentane, but a detailed description is not given since, in general, the same characteristics were observed.

*Reaction at low temperature*. In the experiments of Brunner and Rideal (J., 1928, 1162), carried out at 210°, a large decrease in pressure (15 mm.) was observed during the induction period. Since

this does not take place in pentane, it seemed of interest to investigate the point. A number of oxidations were carried out at this temperature, a 1 : 1 mixture being used at 760 mm. total pressure. In all cases an unmistakable fall in pressure took place, but much smaller than that quoted by these authors. It appeared that this reduction in pressure was due to liquid condensation in the capillary connecting the reaction vessel and manometer. Accordingly, the temperature of this capillary was varied between 40° and 120°. The reduction in pressure during the induction period under these conditions varied in a rather irregular way between 0.8 mm. for the higher temperature and 4 mm. for the lower, indicating, however, a general trend. Hence, this phenomenon is almost certainly not due to absorption of oxygen directly, but rather to the formation of some non-volatile product which condenses in the cooler parts of the system. In all cases of reaction of hexane at low temperatures, a heavy liquid or semi-liquid deposit occurred in the tube : this does not find its counterpart in the case of pentane, nor does it occur with hexane if the reaction takes place at higher temperatures.\*

*Amylene.*—Amylene has been examined in the present apparatus for purposes of comparison with the work of Lewis (J., 1929, 759), and because of its intrinsic interest as a possible stage in the process of the oxidation of pentane.

The fraction of b. p. 36—36.5°/746 mm. was used. The reacting temperature is manifested in a different manner from that with pentane. When a 1 : 1 mixture of amylene and oxygen at 760 mm. total pressure is heated at a rate of 0.6° per min. from 200°, the normal gas curve is followed for a short time, then the pressure begins to fall below it. At 215° this drop in pressure becomes quite sharp, and continues until a minimum is reached at 236°. The depression in pressure is about 50 mm. or 7% of the total. A fairly sharp minimum is registered, after which the pressure rises rapidly, falling off, however, to a normal gas curve at a pressure well below the original at this temperature. At lower fuel concentrations, the drop in pressure is replaced by a period of no pressure change, after which the pressure rises rapidly in a manner similar to that of pentane. This is illustrated in Fig. 1.

Lewis (*loc. cit.*) obtained similar curves, but did not differentiate between the effect of total pressure and of concentration. It will be seen that the two different types of curve are obtained by variation in concentration alone.

If the reaction is carried out at 211.5°, a long induction period occurs during which a steady fall in pressure takes place. A mini-

\* When heptane is oxidised, considerable quantities of a solid resinous product are formed, which condense at comparatively high temperatures.

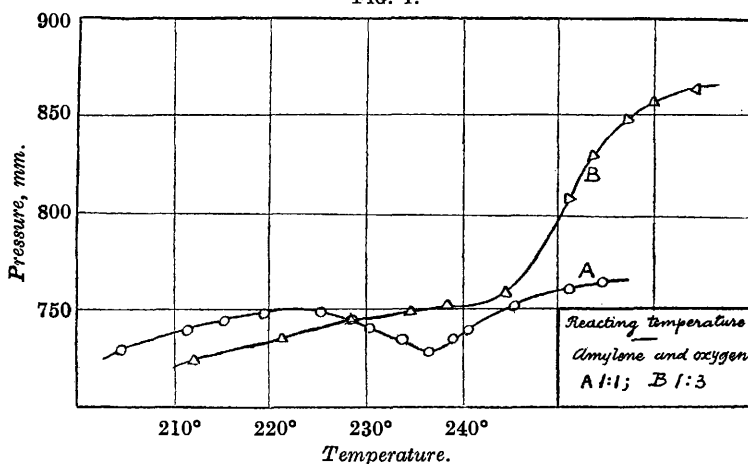
imum is reached when 7.5% of the original volume has disappeared, after which the pressure rises. These variations in pressure make it difficult to follow the kinetics of reaction by noting the pressure variation. There was no evidence in this case of any condensable substance forming in the capillary, and the reduction in pressure is due mainly to direct absorption of oxygen by the unsaturated substance.

The results of the gas analyses are of interest :

$C_5H_{10} : O_2 = 1 : 1$ ; at 760 mm. total pressure

	CO <sub>2</sub> , %.	O <sub>2</sub> , %.	CO, %.	Residue, %.
After complete reaction .....	26.0	7.1	30.1	36.8
At minimum pressure point .....	17.7	38.5	15.0	27.0

FIG. I.

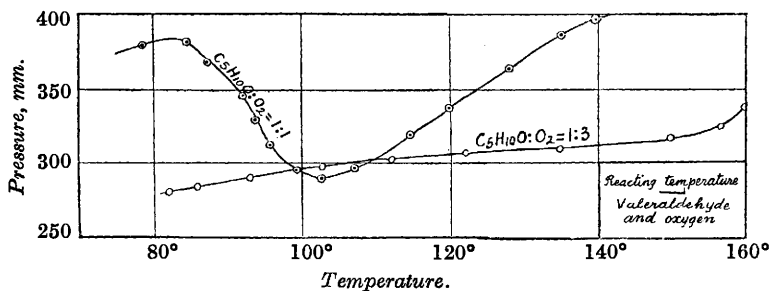


At the point of minimum pressure 67% of the final amount of carbon dioxide has been produced, and about the same amount of oxygen consumed. The rapid drop in pressure is probably caused by the absorption of oxygen, which overcomes the increase of pressure due to the formation of carbon oxides. When, however, there is a large excess of oxygen present the latter process predominates, and the minimum is obliterated. With the 1 : 1 mixture only 33% of the oxygen can be accounted for in the manner described in the preceding paper, indicating the presence of a large percentage of condensable compounds removed by cooling the gas before analysis.

*Valeraldehyde.*—The reacting temperature of valeraldehyde (b. p. 98°/755 mm.) was investigated as in preceding cases. A mixture of valeraldehyde with pure oxygen has a much lower reacting temperature than any of the compounds that have been examined.

A 1 : 1 mixture reacts at 84° in a manner analogous to that described for amylene (see Fig. 2). A drop in pressure takes place to the extent of 25% of the original, after which a rapid rise follows, though the pressure never reaches the original value. Reaction at lower concentrations of fuel is similar to that with amylene: the fall in pressure is obliterated by a rapid increase, the latter process taking place at considerably higher temperature (see Fig. 2). Gas analysis of the end products shows that 80% of the original oxygen may be traced to carbon oxides (largely dioxide) and water, as compared with 42% in the case of pentane. Hence, valeraldehyde is more completely burned than the corresponding hydrocarbon. Coupled with the fact of the initial ease of oxidation, this indicates that the formation of an aldehyde group on the carbon chain in the case of pentane would be a probable early step in the mechanism of oxidation (Pope, Dykstra, and Edgar, *J. Amer. Chem. Soc.*, 1929, **51**, 1875).

FIG. 2.



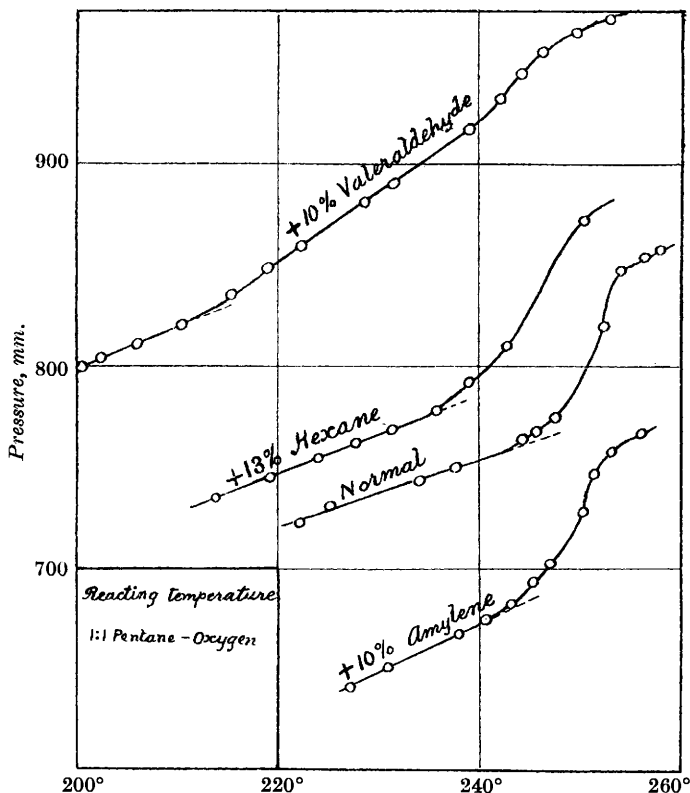
*iso*Pentane and *iso*Amyl Alcohol.—The *isopentane* (kindly supplied by Dr. Mardles) boiled at 31.6°/764 mm. and probably therefore contained some *n*-pentane. The reacting temperature of a 1 : 1 mixture at 800 mm. total pressure was 245° (verified a number of times), *i.e.*, about the same as for *n*-pentane.

Owing to its low volatility, it was difficult to employ a high partial pressure of *iso*amyl alcohol in the apparatus. A 1 : 1 mixture at 600 mm. total pressure did not react up to 280°, at which temperature a mild explosion sometimes took place. At 450 mm. total pressure a 1 : 1 mixture showed no reaction up to 291°: it was not heated above this temperature. Hence it appears that the alcohol is definitely more difficult to oxidise than the corresponding hydrocarbon, under the same conditions of concentration, total pressure, and surface. *n*-Pentane-oxygen (1 : 1) would react rapidly at 250° at 450 mm. pressure.

(b) *Effect of adding a Third Compound to Pentane-Oxygen Mixtures.*—If the combustion of a hydrocarbon proceeds in such a way

that the active molecule combining with oxygen forms an active complex, providing in turn an active product to transmit the chain, the formation of this initial compound depends, among other factors, upon temperature. A certain temperature must be attained in the normal case before there will be enough active centres formed in a given time to exceed the number which are destroyed. Until this takes place the "stationary" state cannot be passed, and the

FIG. 3.



reaction only proceeds slowly at the walls. The temperature at which this more or less rapid homogeneous reaction takes place varies for different compounds, and is clearly influenced by the deactivating surface, and is closely related to the "reacting temperature." Hence, it seemed that the active complex formed during the oxidation of one compound might be able to activate some other similar compound and cause it to react at a temperature at which it is normally unreactive. Thus a small quantity of hexane (reacting

temperature 223°) might be expected to hasten the oxidation of a large amount of pentane (reacting temperature 245°). If this were to happen, it would be additional evidence in favour of the theory of chain reactions as applied to the oxidation of pentane, and might be interesting from the point of view of exchange of activation energy.

Mardles has already shown (J., 1928, 873) that benzene, aniline, etc., can be oxidised at much lower temperatures when present in small quantity with another hydrocarbon undergoing combustion, but this is not quite the same as initiation of combustion of the major part by the presence of a small quantity of a second hydrocarbon which reacts at a lower temperature.

It is also of interest to add compounds which would be expected on the hydroxylation theory to appear during the normal course of slow combustion, in order to ascertain if any one exerted a marked accelerating effect on the reaction as a whole.

The effect of these added compounds on the "reacting temperature" is indicated in Fig. 3 and the following table:

Added compound.	O <sub>2</sub> , mm.	C <sub>5</sub> H <sub>12</sub> , mm.	Added compd., mm.	Reacting temperature.
(Normal) .....	388	382	—	245°
Hexane .....	358	376	111	236
Amylene .....	305	305	68	245
Water .....	380	375	15	245
Valeraldehyde .....	400	405	86	(obliterated)

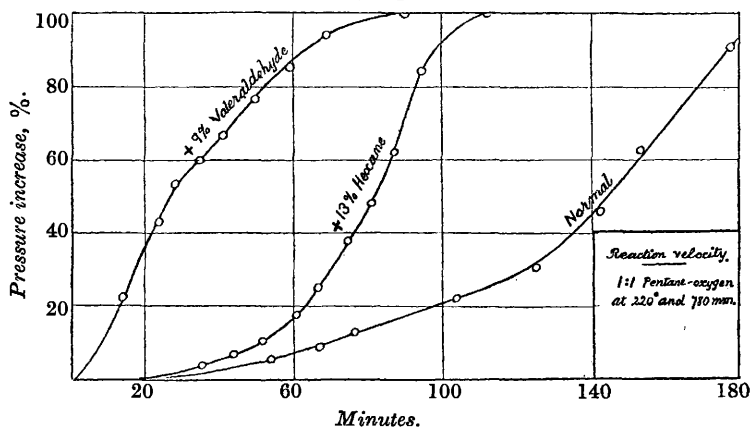
Hexane thus lowers the reacting temperature, but amylen and water vapour apparently have no effect, and valeraldehyde completely removes the sharp inflexion by causing reaction at lower temperatures, but at the same time regulating the later reaction in the manner shown in the accompanying graph. The absence of effect with water is to be expected, as no attempt to produce intensive drying was made; hence it may be assumed that a certain amount of water is present on the walls of the apparatus at all times, and addition of further water is without effect.

The same compounds have been added to pentane-oxygen mixtures at low temperatures to show their effect on the initial stages of reaction. The results (Fig. 4 and following table) again

Compound added.	O <sub>2</sub> , mm.	C <sub>5</sub> H <sub>12</sub> , mm.	Compound, mm.	t <sub>0.5</sub> , mins.	t <sub>0.8</sub> - t <sub>0.4</sub> , mins.
Reaction at 220°.					
(Normal) .....	365	370	—	147	27
Hexane .....	342	336	107	81	18
Amylene .....	378	332	87	(Drop in pressure)	
Valeraldehyde .....	395	395	78	29	32
Reaction at 210°.					
(Normal) .....	397	392	—	(No reaction after 180 mins.)	
Valeraldehyde .....	394	395	75	66	

show the very marked accelerating effect of valeraldehyde: the induction period is greatly shortened, and the subsequent reaction somewhat retarded. It is also interesting that hexane shortens both induction period and subsequent reaction. Amylene seems to exert no effect: from the curve it appears to be oxidised independently of the pentane with consequent reduction in pressure. *iso*Amyl alcohol was also without effect. Valeraldehyde, as well as hastening the initial stages of reaction, causes reaction at temperatures below which it normally takes place. A consideration of the increase in pressure, coupled with results of analysis, confirms the fact that at 210° the pentane has reacted when in the presence of valeraldehyde.

FIG. 4.



Thus it appears that the active products formed during the oxidation of one compound may initiate chain reactions in a second mixture which, if the conditions are suitable, may lead to reaction of the mass of the gas.

This effect of aldehyde is by no means an isolated observation. Bone and Hill (*Proc. Roy. Soc.*, 1930, **129**, 434) have stated that acetaldehyde added to a reacting mixture of ethane and oxygen will cause explosion. It is probable that the ease with which acetaldehyde forms a peroxide is the reason for its activity (Bowen and Tietz, J., 1930, 234).

In conformity with a suggestion (Egerton and Gates, *Aer. Res. Comm.*, R. & M. 1079, 1926) regarding the effect of "anti-knock" compounds, which greatly raise the igniting temperature of aldehydes, the products of combustion of an aldehyde were held to be partly responsible for the catalysis of the hydrocarbon combustion. The inhibitor became effective in preventing the formation of these

products by retarding the oxidation of the aldehyde.\* The aldehyde was produced by the decomposition of the initially formed peroxide, and was present in small concentration. There were reasons against this view, for aldehydes added to petrol have not been found to act as potent pro-knocks. In the case of slow combustion, however, the suggestion is supported. Further investigations are being made on this point.

The negative effect of amylene may be regarded as evidence against the theory of dehydrogenation of the molecule prior to reaction (see Lewis, *loc. cit.*; Berl, Heise, and Winnacker, *Z. physikal. Chem.*, 1928, **139**, 453), for the oxidation of this unsaturated compound apparently does not produce an initial complex which is able to catalyse the oxidation of pentane, while the behaviour of *isoamyl* alcohol is not such as would be expected if it formed an essential early stage in the reaction.

It is difficult enough to ascertain the exact course of the reaction of a hydrocarbon such as ethane, but in the case of the higher hydrocarbons, the possible complications are far greater, and what happens in the case of the lower hydrocarbons is not necessarily followed by the higher members. The present experiments do not purport to do more than indicate certain features of the process of oxidation, and to point the way to further investigations.

*Note on the Action of Lead Tetraethyl during the Oxidation of Pentane.*

It has been shown (see Egerton and Gates, *loc. cit.*) that lead tetraethyl raises the self-ignition temperature of pentane-air mixtures, the effective part of this inhibitor being the metal radical. Numerous colloidal metals have been tried, and several found effective; even the vapour of potassium was very effective. Under the conditions of those experiments, it was certain that the potassium was oxidised before reaching the reaction vessel. Hence it was the oxide which was effective in inhibiting the oxidation. This suggested that all metals which were effective in this connexion acted in an incipient state of oxidation. The idea was further strengthened by the observation that most of the metals which were effective could exist in two states of oxidation, the equilibrium temperature being approximately that at which the inhibitor is effective.

In view of the fact that the metallic oxide, to be effective, must be present in the molecular condition, it is difficult to prove the point, and some investigators have found that the oxides (*e.g.*, lead oxide) are ineffective (almost certainly because insufficiently dis-

\* But not only the aldehyde, because aldehydes did not accumulate, and the initial hydrocarbon oxidation was also thought to be inhibited (*Nature*, Supplement, July 7, 1928).



perse). The work now to be described provides direct evidence that the inhibitor must be oxidised before it is effective.

*Apparatus.*—Certain alterations were made to the apparatus. A separate line was added between the reaction vessel and the evacuating system, so that the products of combustion could be removed without contaminating the rest of the apparatus. In spite of this precaution, the apparatus soon becomes contaminated, and it is necessary to dismantle it completely for cleaning.

The lead tetraethyl was added from a tube containing the liquid, which was sealed on below the ground joint *G* (see Fig. 1 of Part I). The vapour first passed into a small bulb of about 5-c.c. capacity, and when this was placed in communication with the reaction vessel, the resultant equalisation of pressure gave an amount of lead tetraethyl equal to about 0.1% of the total mass of the reacting gas. In the normal course, the inhibitor was added to the heated bulb before the mixture of pentane and oxygen. It was also possible to add oxygen to the inhibitor, and to heat the mixture so formed for a short time before the addition of the reacting mixture.

The following standard conditions were chosen : a 1 : 3 mixture of pentane : oxygen at a total pressure of 400 mm. was added to the chamber at a constant temperature ( $265^{\circ} \pm 0.1^{\circ}$ ); Pyrex bulbs of approximately 80-c.c. capacity were used as the reaction vessels.

*Results.*—The effect of the addition of lead tetraethyl under various conditions to oxygen-pentane mixtures is indicated in Fig. 5 and below :

O <sub>2</sub> , mm.	C <sub>5</sub> H <sub>12</sub> , mm.	<i>t</i> <sub>0.5</sub> , mins.	<i>t</i> <sub>0.8</sub> - <i>t</i> <sub>0.4</sub> , mins.	
309	108	19.8	4.2	Average of a large number of determinations.
309	112	10.7	3.7	PbEt <sub>4</sub> added before mixture.
310	110	55.7	11.2	PbEt <sub>4</sub> oxidised for 7 mins. before addition of mixture.

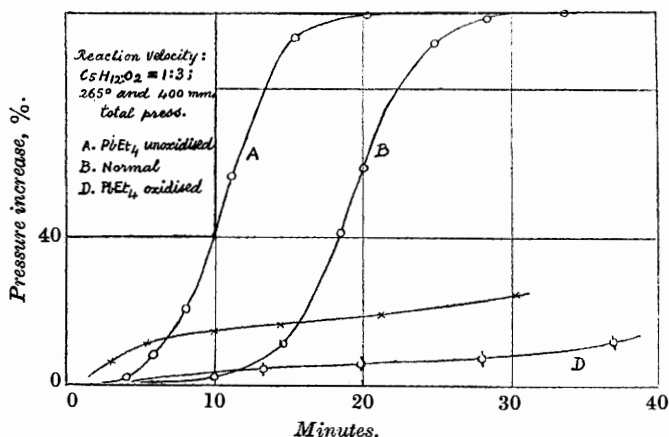
When the lead tetraethyl is added alone, the reaction of the pentane is somewhat accelerated, but when it is oxidised before the reacting mixture is added, the resulting reaction is strongly retarded.

After a number of experiments which yielded results similar to those shown above, the apparatus became contaminated, so that when the lead tetraethyl was added, the reactions were inhibited in all cases, even when it did not receive preliminary oxidation. The reactions under these conditions followed the type indicated by  $\times$  in Fig. 5. The initial acceleration took place, but the reaction was immediately inhibited. The products of combustion of the lead compound from previous experiments still appeared to be exerting their inhibitory effect. These substances must find their way into the reacting chamber in very minute quantities, coming from other

parts of the apparatus, for the bulb and capillary were washed with boiling chromic acid after each experiment.

The apparatus was completely reconstructed before normal runs could be again obtained. In later experiments it was not possible to repeat the accelerating effect of the inhibitor when first added, though before preliminary oxidation it exerted very little effect either way. After preliminary oxidation, however, the powerful retardation was immediately obtained. It is possible that the accelerating effect is due to the ethyl radicals, but this has yet to be proven; it may be an effect on the walls of the vessel. It must be pointed out that once the reacting mixture is added, oxidation of the lead can commence; so that the accelerating effect would not be likely to persist.

FIG. 5.



These experiments provide direct evidence that the lead must first be oxidised before it is effective as an inhibitor.

#### Summary.

(i) In the slow combustion of hexane, amylene, valeraldehyde, and *iso*amyl alcohol, the temperature at which oxidation becomes rapid, and the influence of total pressure and concentration on the reaction have been noted. The decrease in pressure in the case of hexane is mainly due to formation of a condensable product, but in the case of amylene to direct absorption of oxygen.

(ii) The influence of these compounds on the oxidation of pentane has been determined. Active hexane is able to initiate reaction in pentane mixtures at lower temperatures than would be the case in pentane-oxygen alone, and valeraldehyde is still more effective. Amylene and *iso*amyl alcohol, on the other hand, are ineffective.

These facts do not accord well either with primary dehydrogenation of the reacting molecule or with hydroxylation.

(iii) Lead tetraethyl acts as an inhibitor, but the lead has to be oxidised before being effective.

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[*Received, December 19th, 1931.*]

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