CCLXXXVI.—*Low-Temperature Oxidation. Part III. The Lag in Ignition of Some Hydrocarbons.*

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Ignition temperatures are considered important characteristics in the study of fuels and certain inflammable materials, and a brief summary of the experimental methods by which comparative data are obtained was given in Part II (this vol., p. 58). Certain anomalous results were pointed out, such as the ignition temperature of octane being lower than that of *iso*decane, and it was suggested that the lag in ignition might be preferable as a comparison of the ignitability of the hydrocarbons. The experiments must be identical in respect of apparatus, temperature, and molecular concentration.

The lag is usually defined as the interval of time between the rapid heating of the mixture to or above a certain minimum temperature, called the ignition point, and the appearance of flame. Many variables must be considered in its measurement. It is a function of the concentration, temperature, the nature, extent and history of the igniting surface, the manner in which the mixture is presented to the heated surface, and possibly the diameter of the tube or bulb. In the case of the paraffins the lag increases with decrease in molecular weight. Most of the foregoing points have been studied by

Mason and Wheeler, who have reviewed the subject of lag in their papers (J., 1922, **121**, 2070; 1924, **125**, 1869).

It appears advisable to apply the phenomenon of lag to the study of pinking or detonation in internal combustion engines. During pinking the unburnt mixture ahead of the original flame may ignite spontaneously, giving rise to a high rate of release of energy. This will be minimised by an increase in the flame rate, *e.g.*, by turbulence, or a decrease in the distance to be travelled by the flame, or a prolongation of the lag under the actual conditions of temperature and pressure, etc., encountered in the cylinder, and the last will be dependent on the nature and condition of the surface or the presence of anti-knocks or pro-knocks. These reagents must also be operative under the prevailing conditions in the cylinder.

The term pre-flame period which is used in connexion with ignition temperatures is subject to modification, since the lag may terminate in a rapid oxidation unaccompanied by flame. Such results are obtained by maintaining the mixtures at a constant temperature somewhat lower than the observed ignition point, or by the presence of an oxidising agent even at temperatures well above the ignition point (see Part II), and the author views the results of Brunner and Rideal (J., 1928, 1162) as examples of extremely long lag.

The present paper gives other examples of oxidation without ignition at high temperatures, below which flame does not appear.

EXPERIMENTAL.

The lag interval has been determined by three methods, (i) adiabatic compression of the mixture (Tizard and Pye, *Phil. Mag.*, 1922, **44**, 79; 1926, **1**, 10, 94); (ii) evacuated bulb experiments in which the explosive mixture is rapidly indrawn at a suitable temperature, the interval between the times of filling and ignition being regarded as the lag and recorded graphically on a revolving drum (Mason and Wheeler, *loc. cit.*); (iii) the "crucible" method, in which the time between the fall of the liquid drop and the appearance of flame is measured (Moore, *J. Soc. Chem. Ind.*, 1917, **36**, 110).

A variation of method (ii) was tried in which the weighed quantity of liquid hydrocarbon, in a sealed tube drawn out to a capillary, was put into the bulb and after evacuation of the bulb the capillary was broken, the bulb thus being filled with vapour : at the experimental temperature, air was allowed to rush in through a non-return valve. The results, however, were not satisfactory, since the mixture often failed to ignite or only did so at a much higher temperature than the observed ignition temperature. This may have been due to the surface being coated initially with a hydrocarbon film, and it may be recalled that Mason and Wheeler found it necessary to enclose nitrogen in their bulbs prior to an experiment before concordant results could be obtained.

Method (iii) has the advantages that a large number of experiments can be carried out in the minimum time and the period of lag near the ignition point is considerable. The following account contains an analysis of this method, the object being to secure in the first instance comparative or qualitative data. It is hoped to study the other methods in the future.

Glass bulbs (125 c.c.) with a long narrow neck were maintained at the desired temperature and the liquid was introduced in small wide-mouthed tubes of thin glass; these were of such length that the amount of liquid that gave the minimum lag by trial and error at a particular temperature just filled them to the brim. All the bulbs were cleaned and steamed, and thoroughly dried before each determination. It is essential that the bulbs be treated in a similar manner, since very variable lags and ignition temperatures are obtained when they are rinsed out with dilute solutions of substances such as potassium dichromate, nitrates of sodium and lead, sodium hydroxide, etc., and dried without washing. Nor is it possible to carry out more than one experiment in a bulb, because the film of the products of a previous experiment increases the lag. Finally it is essential that new bulbs be seasoned, since they give an unduly long lag at the lower temperatures until they have been used and cleaned. Some of the experimental findings are given below.

Glass.—The effect of the smooth surface area has been studied by Mason and Wheeler (*loc. cit.*). A curious phenomenon in the bulb method is the fading away of spontaneous ignition at some particular temperature which is determined by the conditions of the experiment and the nature of the hydrocarbon. As the temperature rises, the ignition point is first reached and flame appears; considerable oxidation, however, may take place below this temperature. The lag is considerable at this stage in the case of the paraffins, but it becomes shorter with rise of temperature until it approaches zero; the report and flash on ignition are then fainter. Finally, the hydrocarbon fails to ignite once more. The point at which this occurs is determined by the molecular weight of the hydrocarbon, the weight of liquid, the diameter and volume of the vessel, and the action of various surfaces and catalysts. By using a test-tube (7 inches × 1 inch) and a droplet of constant size, the following maximum ignition temperatures were obtained, but it must be emphasised that both the lowest and the highest ignition point vary with the diameter of the tube.

Hydrocarbon	$C_{10}H_{22}$	C_9H_{20} (tech.)	C_8H_{18}	C_7H_{16}	C_6H_{14}
Temperature	250°	285°	318°	365°	415°

An analysis of the contents of the bulbs after the experiments showed that the hydrocarbons were considerably oxidised, and the phenomenon is another case of flameless combustion. It is essential that the tubes and bulbs be evenly heated, *e.g.*, in a well-stirred oil-bath, otherwise the ignition failure may not be attained on account of the temperature gradient which is possible in an electric furnace. Presumably, diffusion and rate of oxidation are the important factors, for the fading temperature can be lowered if the hydrocarbon is dropped into the air kept in motion by stirring. When a droplet falls into a heated tube or bulb a certain interval elapses before the liquid vaporises and attains the bath temperature. Meanwhile inter-diffusion of the oxygen and the combustible is taking place and also chemical action. At the ignition point, the rate of oxidation may be comparatively slow, thus permitting by diffusion a high concentration of oxygen and hydrocarbon. By virtue of this increased concentration, the oxidation becomes more rapid and finally results in flame. The mechanism of these reactions has been discussed in Part II. A rise in temperature above the ignition point will increase the rate of oxidation and it is suggested that eventually this may be so great that the components never attain by diffusion the minimum concentration essential for the production of flame but are rapidly oxidised. If this is correct, any agency which promotes oxidation should lower the temperature at which ignition ceases, and the converse should hold good.

The foregoing constitutes a serious objection to the crucible method for the determination of ignition temperatures and lags, but the ignition fading temperature is undoubtedly a measure of the oxidisability of these hydrocarbons, and is a better comparative test than the ignition point. The fading points are in the same order as the lags, which in turn are a function of the molecular weight in the case of paraffins. Thus decane has a higher ignition temperature than octane but a shorter lag at a specified temperature and a lower fading temperature. Although octane ignites at a lower temperature, it must be pointed out that at the first sign of ignition of decane its lag is shorter than that of octane at the same temperature.

The determination of the ignition temperature by the drop method has been instituted as a test for petrols, but in view of the above too much importance cannot be attached to it because of the tendency of the heavy constituents, which are mainly responsible for knocking, to oxidise without flame (compare *iso*decane). Variation in ignition temperature and lag is shown by a petrol when the light and the heavy constituents are removed by distillation.

A commercial petrol was treated for the removal of aromatic hydrocarbons, washed, dried, and distilled:

I. P. T. Specifications.

Initial b. p.	Final b. p.	% distilled at					
		50°.	75°.	100°.	125°.	150°.	175°.
37°	200°	3	16	37	60	75	87

The petrol was progressively distilled and the ignition temperature of the residue and the lag at 290° were determined. With the removal of the lighter fractions, the lag continuously decreased, but the ignition temperature fell at first, remained more or less constant whilst 20—40% was removed, attained a minimum after approximately 80% had been removed, and then began to rise again.

% Petrol distilled	0	5	10	20	30	40	60	80	90	95
Ign. temp. of residue	262°	260°	256°	252°	252°	251°	247°	243°	249°	255°
Lag of residue (secs.)	9·6	9·2	8·6	8·3	8·0	7·6	5·8	4·0	2·4	2·0

The ignition temperatures and the lags at 290° of the distillates from 60% upwards were also determined.

% Distillate	60	70	80	90	95	100
Ign. temp.	292°	279°	270°	263°	263°	262°
Lag at 290° (secs.) ...	—	19·6	12·0	10·8	10·0	9·6

The figures indicate that removal of the lighter constituents of the petrol results in an appreciable drop in lag and in ignition temperature. This is according to expectation and the petrol product will in all probability " knock " more readily as the ignition temperature is lowered. The knocking tendencies of a fuel are associated with the heavy constituents, and their removal improves the quality of a petrol. This improvement was not registered by a rise in ignition temperature in the above experiments, since there was a change of only 1° when the last 10% of the petrol was removed by fractional distillation. On the other hand, the lag was appreciably increased.

The ignition temperature of a petrol determined by the drop method, therefore, cannot be utilised as a measure of the knock rating, because it does not vary sufficiently with the presence or absence of the so-called heavy ends. More useful evidence may be obtained if it is taken in conjunction with the lag, and with the maximum ignition temperature, which appears to be a measure of the rate of oxidation of the paraffins. The latter has been determined for a few commercial petrols and it varies as the time of lag. It is hoped to conduct these experiments with petrols of known knock rating.

The ignition temperature is known to be very sensitive to the presence of catalysts, and promoters of oxidation when present in fairly large proportion raise the ignition points of the substances investigated in Part II. The same substances lower the temperature at which ignition ceases and it may be argued that, if they are sufficiently active and concentrated, they may prevent ignition in a bulb throughout the entire range, although the hydrocarbons will be completely oxidised. Such results were obtained with octane and decane, as the following experiments show.

Powdered Glass.—This increases the extent of the surface and its action on the paraffins depends on its weight and its disposition, *i.e.*, whether it remains compact at the bottom of the bulb or dusted over the whole surface, or is suspended momentarily through the reacting gases by shaking of the bulb just prior to the experiment. Apparently the ignition point is raised and the "fading" temperature is lowered, both of which result from enhanced oxidation. At first the lag is longer than in the case of a plain bulb, but at higher temperatures the time available for the conduction away of the heat of the preliminary oxidation becomes continuously shorter, and the conditions will then be such as to give a shorter lag in the presence of the powder. The following are typical results for *n*-octane and 0·5 g. of powdered glass dusted over the surface of a 125 c.c. bulb.

Temp.	225°	235°	245°	270°	290°
Lag (plain bulb), secs.	22·2	10·0	5·8	3·0	2·0
Lag (powdered glass), secs.	36·2	14·7	7·7	3·0	1·6

At 300° the octane would not ignite in the presence of powdered glass.

Charcoal.—The above actions are more marked in the presence of this substance, and are controlled by the weight and activity of the sample used. It is also a very difficult matter to obtain concordant results with charcoal, since it is more sensitive than powdered glass to disposition. For instance, a given weight of charcoal may prolong the lag, but if it is shaken up or disturbed just prior to the addition of the hydrocarbon no ignition occurs at the same temperature. By using only 0·05 g. of powdered wood charcoal and *n*-octane, considerable extension of the lag may be obtained at lower temperatures.

Temp.	250°	260°	270°	280°
Lag (blank), secs.	5·2	3·6	3·0	2·8
Lag (charcoal), secs.	26·8	15·0	11·6	9·6

Ignition failed at 295° in the presence of this weight of charcoal. It was found possible to inhibit spontaneous ignition throughout the range by using 0·5 g. of decolorising charcoal and stirring it up with a puff of air just before the addition of the octane. Undoubtedly the weight of charcoal employed was far too great: by reducing the weight to about 0·005 g., results similar to those for powdered glass were obtained and the lag at 255° was actually shortened.

Metals.—The catalytic activity of a metal is dependent on the condition of the surface, *e.g.*, the fineness of the grain structure, the crystalline structure presented, oxide film, or amorphous layer due to polishing. The experiments described below, however, are only qualitative and were made to determine the action of metals on the lag. It was shown in Part II that, contrary to expectation, those metals which promote oxidation raise the ignition temperature. This result suggests a corresponding increase of lag, and it was thought that it might be possible to obtain some indication of this if strips of metal were present in the bulb.

(a) *Copper.* Freshly cleaned and polished sheet copper has little action on the lag. The copper sheet was cut into strips of 8 × 0·5 cm. and inserted into the bulb just prior to the hydrocarbon. There was a tendency to prolong the lag at low temperatures, especially when several strips were used, but with rise of temperature there was apparently no difference between the blank and the copper experiments. On the other hand, when the copper had not been polished, or had been passed through the oxidising portion of a Bunsen flame and so coated with an oxide film, its activity in raising the ignition temperature and in extending lag was increased. Copper gauze is particularly active, especially when the surface has been activated by repeated oxidation in air and reduction in hydrogen. A strip of gauze (15 × 0·7 cm.) so treated raised the ignition point of octane to 260° and at 270° the lag was 18·2 seconds, and two such strips entirely prevented ignition.

As in the case of powdered charcoal and glass, the temperature coefficient for a copper surface is much greater than for a plain glass surface, and therefore at higher temperatures the lag at a copper surface may be shorter than at a glass surface. Copper test-tubes (6 ins. × 1 inch) were used in making this comparison. A set of test-tubes was prepared and cleaned in an identical manner, inserted in a bath 60 seconds before the test, and used once—since a second experiment in the same test-tube after expulsion of the contents always gave a shorter lag. The following results indicate the temperature–lag changes for (1) a plain glass surface, (2) a new copper surface, and (3) a copper surface used once. A new copper surface at low temperatures prolongs the lag, but at temperatures approaching 285° the lag is reduced.

Temp.		230°	240°	260°	280°	285°
(Octane) Lag in secs.	(1)	15·0	8·6	4·8	2·8	2·2
	(2)	42·0	41·0	11·8	2·0	No ign.
	(3)	28·0	15·0	10·0	3·0	2·6

(b) *Lead.* The qualitative results for lead are substantially the same as those for copper. A freshly cleaned and polished surface appeared to have little more action than a glass surface, unless present in appreciable amount. The ignition temperature of octane was slightly higher in the presence of two strips of polished lead and the lag was somewhat longer at temperatures just above this point, but with rise in temperature the difference decreased until at 260° the lags were practically identical.

The activity of an old lead surface obviously coated with a film of oxide was much greater, and with two strips as above the ignition occurred above 245° after an extended lag. If the experiments are carried out in a test-tube (7 × $1\frac{1}{2}$ in.), a strip of lead foil (6 ins. × $\frac{1}{2}$ inch) is sufficiently active to inhibit ignition completely.

Experiments were made with finely divided lead obtained by the reduction of lead oxide in the bulbs. These were evacuated and the mixture of air and octane (20%) was allowed to enter suddenly. No ignition was obtained up to 300°.

(c) *Aluminium.* In this case the freshly cleaned surface is more active than an unpolished surface which carries an old oxide film. The former displays great activity in raising the ignition point and prolonging the lag at the lower ignition temperatures when the quantity of metal present is small, and with somewhat larger surfaces the auto-ignition may fail altogether. For instance, with one strip of aluminium (9 × 0·5 cm.) the changes in lag for octane were as follows :

Temp.	230°	240°	250°	260°	270°	280°
Lag (blank), secs.	13·2	8·6	5·0	3·8	3·0	2·6
Lag (aluminium, unpolished)	15·8	9·3	6·4	4·5	3·0	2·6
Lag (aluminium, cleaned)	No ign.	15·0	7·0	4·6	3·2	2·4

Four strips of aluminium of the above size will inhibit ignition through the whole range up to the fading temperature in glass alone. This is well illustrated by carrying out the experiments in test-tubes. A single strip, if flat, raises the ignition temperature with the usual prolonged initial lag. A similar strip, but corrugated so that the metal surface in the hydrocarbon vapour is enlarged, prevents auto-ignition.

(d) *Other metals.* Those metals which do not promote the oxidation of hydrocarbons or which have slow action, *e.g.*, zinc and tin in the form of polished strips, appear to have little effect on the ignition temperature and lag. On the other hand, metals which promote the oxidation of hydrocarbons tend to raise the ignition temperature under the above conditions of experiment. At first the lag is considerably extended; this, however, is a matter of temperature, because at much higher temperatures the lag interval is reduced. The condition and extent of the metallic surface are of importance, as in the case of aluminium and copper, and one would expect smooth platinum foil to be far less active than the same strip coated with platinum-black. Experiment confirms this opinion: the results were much the same as for polished and etched copper surfaces. Iron belongs to the same category. Further, a thin wire of an active metal such as copper, aluminium or platinum, which will affect the lag only slightly when stationary, produces an extended lag when stirred in the mixture after the addition of the hydrocarbon droplet, and more rapid stirring entirely inhibits auto-ignition.

Metallic Oxides.—The ignition temperatures of octane in oxygen in the presence of various metallic oxides were first determined by the method employed in Part II, 30% of the hydrocarbon and 0·2 g. of oxide being used. The oxides were prepared by the ignition of the hydroxides at as low a temperature as possible. The following results were obtained with the same rate of heating:

Oxide	Al	Cr	Zn	Sn	Fe	Pb	Cu
Temp.	218°	217°	216°	216°	nil	nil	nil

No explosion occurred in the presence of the last three oxides; extensive oxidation, however, had taken place, because the bulbs became about two-thirds filled when opened under water, the residual gases being carbon dioxide and monoxide. There were also marked colour changes in the surfaces of the oxides of lead and copper, the latter acquiring a reddish tint and the former darkening to the colour of lead dioxide.

The determination of the lag interval in the presence of powdered oxides presents the same difficulties as in the case of powdered glass, the time being dependent on the disposition of the active material, *e.g.*, whether dusted over the surface of the glass or resting as a compact mass at the bottom. Reproducible results are hard to obtain and a constant weight of oxide may give widely varying times of lag.

The procedure adopted was to commence with a large weight of the oxide, *e.g.*, 0·5—1·0 g. In the case of the active oxides, complete inhibition of ignition could be obtained, especially when the powder was agitated by a gentle puff of air to give a suspension in the air and a deposit over the glass surface. By gradually reducing the weight of oxide, an amount could be arrived at which appreciably raised the ignition point and extended the lag. At higher temperatures the same weight gave lags which approached, or were even shorter than, those for the plain glass surface. The maximum self-ignition temperature was also lowered (compare powdered glass). A further reduction in the weight of oxide appeared to lower the temperature at which the lag was shorter than that for the plain glass surface, until finally, with only a trace of oxide, the lag was considerably reduced at comparatively low temperatures. The results for heptane and copper oxide at 293° are typical.

Wt. of oxide (g.)	0	0·5	0·14	0·05	0·001
Lag (secs.)	10·0	No ign.	16·0	12·0	5·2

The oxides used in the above experiments displayed varying degrees of activity and may be placed in the following descending order : lead, iron, copper, aluminium, tin, and zinc.

Pro-knock Reagents.—It has been established that certain unstable and active oxidising substances when introduced with the fuel into an engine cylinder induce detonation or knocking. These include alkyl nitrites, organic peroxides, nitrogen peroxide (Mardles, J., 1928, 872), and probably ozone. The same investigator states that the ignition temperatures of *n*-butyl alcohol, xylene, and ethyl alcohol are lowered proportionately by these substances. These fuels have comparatively high ignition points, above 500°. The results are entirely different with the hydrocarbons which ignite at about 300°, *e.g.*, the normal paraffins from pentane to decane, and, again, the important factors of the conditions of experiment, such as temperature, concentration, etc., must be noted. The following experiments establish the fact that the above-mentioned active reagents may raise the ignition point of the paraffins and petrols and at the lower temperatures the lag is considerably increased.

Nitrogen peroxide. Different quantities of this catalyst were added to the air in 125 c.c. bulbs by expelling the gas from capillaries of different lengths to yield the approximate composition required. This oxide of nitrogen is extremely active in retarding auto-ignition, and octane containing 1·0% of it will not ignite below 300° ; moreover, the lag is considerably prolonged when the percentage of oxide is reduced to such a proportion that it will permit of ignition below 300°. The lag for *n*-octane at 260° is 16 seconds in the presence of 0·1% of nitrogen peroxide and 3·6 seconds in the blank test. An increase in the concentration of the peroxide brings about a correspondingly longer lag; *e.g.*, at 270°, *n*-octane gave the following times :

% NO_2	0	0·1	0·2	0·3	0·4	0·5
Lag (secs.)	3·0	6·4	7·8	14·0	25·0	No ign.

Similar results were obtained for *n*-heptane at 300°. Experiments conducted with ether, which has a low ignition point, showed that small concentrations of nitrogen peroxide below 1% had little effect on the ignition point, but with concentrations of the order of 2—3% the ignition temperature was raised several degrees and the lag was slightly increased. From what has been stated above, one might expect that the lag would be decreased by this catalyst at a much higher temperature or by much smaller concentrations.

The action of 0·1% of nitrogen peroxide on *n*-octane at temperatures up to 300° was as follows :

Temp.	260°	270°	280°	290°	300°
Lag (secs.)	16·0	6·4	3·0	2·0	No ign.

As in the case of the active oxides, by a reduction of the nitrogen peroxide content to extremely small proportions the time of lag can be made shorter than that of the blank test at temperatures slightly above the ignition point in glass.

Amyl nitrite. This reagent must be placed in a different category in that it has a definite ignition point of its own which is well below 300° : Ignition temperature = 248° ; lag = 4·0 seconds.

It must also be included in that class of substance whose lag interval is short even at the first indication of spontaneous ignition, *e.g.*, ether. Such substances undergo considerable oxidation or decomposition at considerably lower temperatures—without the appearance of flame. In a study of the effect of amyl nitrite on the lag time and the ignition temperature the foregoing must be considered.

The ignition temperatures of *n*-octane and decane were considerably raised by amyl nitrite and the lags were prolonged at temperatures below 250°, but at some temperature above the ignition point of amyl nitrite, depending upon the concentration of the latter, the lag intervals were actually decreased. On the other hand, the ignition point of hexane, which is well above the ignition temperature of amyl nitrite, was lowered by the latter and the lag period was shortened. The following results represent the effect of 2% of amyl nitrite in *n*-octane under comparable conditions :

	Temp.	230°	240°	250°	260°	270°	280°
n-Octane.	Lag (secs.)	42·0	15·0	9·0	5·6	4·0	2·8
n-Octane + 2% of amyl nitrite.	,, ,,	No ign.	22·8	11·8	4·5	3·2	1·8

Anti-knock Reagents.—These are substances which are added to the fuel to inhibit the undesirable pinking or detonation in petrol engines, and the majority of the published results show that they have a marked action in raising the ignition temperature. This does not distinguish them from the pro-knocks where petrols are concerned (Part II). It was supposed that knock suppressors were anti-oxidants, but many of the latter substances, such as quinol, are of no service in petrols, and it does not follow that a catalyst which is negative at the ordinary temperature will so function under the conditions obtaining in the engine during the explosion. There is evidence, however, that the two classes of substances known as knock inducers and suppressors do act differently on the rate of oxidation of hydrocarbons at temperatures below the ignition points, the latter having marked inhibiting properties. A résumé of this subject has been given by Schaad and Boord (*J. Ind. Eng. Chem.*, 1929, 762).

Lead tetraethyl, the most efficient anti-knock, does not greatly inhibit oxidation at the ordinary temperature in comparison with anti-oxidants such as quinol. The success of the former in internal combustion engines is reputed to be due to its decomposition products (Egerton and Gates, *J. Inst. Pet. Tech.*, 1927, 244; Souders and Brown, *J. Ind. Eng. Chem.*, 1929, 1261). The former workers report that decomposition begins at 230°. Many hypotheses have been put forward to explain the action of lead tetraethyl, the majority of them being concerned with the lead produced by dissociation, but these cannot explain why lead tetraethyl, triethyllead chloride, and diethyllead dichloride have relative efficiencies as knock suppressors in the ratio of 4 : 3 : 2 (Church, Mack, and Boord, *J. Ind. Eng. Chem.*, 1926, 334). Undoubtedly the ethyl radicals play an important part and it is significant that the xylenes, which are theoretically capable of splitting off two methyl groups, are more effective than toluene with one group, which in turn has a better knock rating than benzene (Howes and Nash, *J. Soc. Chem. Ind.*, 1930, 16T). These free organic radicals, however, are reported to be promoters of oxidation.

In the drop or crucible method the concentration of lead tetraethyl necessary to prevent the appearance of flame is exceedingly small, especially for the paraffins of high molecular weight. Octane containing 0·1% of it will not ignite in a bulb or test-tube with an open mouth, although a sudden pressure rise without flame can be obtained after a prolonged lag when the mouth is closed as described in Part II. With concentrations that permitted ignition it was found that (1) the ignition temperature was raised and the lag prolonged, (2) only one experiment could be made in a bulb or tube, because, even after the residual gases had been blown out, the glass surface was coated with an active film, presumably of lead oxide, which sometimes increased the lag but usually prevented further ignition at the same temperature. The results for hexane were :

	Temp.	285°	297°	310°	317°
Hexane.	Lag (secs.) ...	22·0	12·8	9·2	6·0
Hexane + 0·1% $PbEt_4$.	„ „ ...	No ign.	23·0	15·5	10·8

Aniline is typical of the non-metallic compounds which act as knock suppressors, but in comparison with lead tetraethyl much greater concentrations are required. The addition of 0·1% has a negligible effect on the lag, but with ten times this concentration the ignition temperature is raised and also the lag is increased in all experiments up to the highest temperatures at which ignition takes place.

As far as the results obtained by the crucible method are concerned, the rates of change of lag with temperature in the presence of these anti-knock reagents are far less than the rates produced by the promoters of oxidation, and it will be necessary to make more exact comparisons by one of the other two methods of determining lag.

Counter-effects.—In crucible tests the promoters and the inhibitors of knocking can increase the lag and raise the ignition temperature of paraffins, but in the case of the former the change of lag with rise of temperature is very rapid and by reducing the quantity of the catalyst and raising the temperature it is possible to reduce the time of lag below that of the blank test, *i.e.*, to accelerate the lag. This has not been found possible with the inhibitors. Now the efficacy of lead tetraethyl in the internal combustion engine has been ascribed to the oxidising action of the lead particles, which act as miniature sparking plugs ahead of the flame front and so produce uniform combustion (see Church, Mack, and Boord, *loc. cit.*). The theory is a very attractive one, but in the light of the above experiments with aluminium, lead, etc., one would substitute the idea of flameless combustion for active combustion ahead of the flame front induced by lead particles and ethyl radicals. However, in their effect on oxidation and also on ignition and lag the two classes of substance are apparently distinct and when a member of each is present they oppose each other. It is known that ether nullifies the effect of lead tetraethyl in petrol and it has been shown in Part II that the ignition temperature of a hydrocarbon which has been raised by lead tetraethyl may be lowered by the presence of an oxidising surface of powdered glass or pumice. Interesting results were obtained with nitrogen peroxide and lead tetraethyl. The oxide of nitrogen was added to the air in a bulb in such quantity that no ignition of octane occurred at 260° or only took place after a long lag. When the experiment was repeated with octane containing 0·04% of lead tetraethyl, which also prolongs the lag, ignition occurred very readily and the lag was considerably reduced; in fact, in some experiments in which both catalysts were present the lag was shorter than in the blank test, as the following typical result shows:

Reagent	Blank.	NO_2(0·1%).	$PbEt_4$.	Mixture.
Lag (secs.)	3·6	18·0	No ign.	3·2

Similar results were obtained with amyl nitrite and lead tetraethyl, but in this case both reagents were dissolved in the hydrocarbon.

The former at temperatures approaching 300° readily diminished the lag and in experiments carried out with heptane it was found possible gradually to lengthen the lag of a solution containing 2·0% of amyl nitrite by additions of a solution containing lead tetraethyl or aniline.

Summary.

Experiments on the lag in ignition of hydrocarbons have been made by a variation of the drop or crucible method. The results indicate that the lag is to be preferred to the ignition temperature as a test of the ignitability of paraffins and petrols, since it is a function of the molecular weight or the boiling range. In this method the rate of diffusion apparently plays an important part, since the hydrocarbon may be removed by oxidation and without flame almost as quickly as it diffuses into the oxygen, thereby withholding spontaneous ignition. The rate of oxidation increases with molecular weight in the case of the paraffins; for instance, decane has a higher ignition point than octane, and a kerosene fraction has a higher one than petrol in crucible experiments. Substances which promote oxidation have been shown to raise the ignition temperature and increase the time of lag, but by reducing the proportion of some of them to a minute amount and raising the temperature, the time of lag has been diminished. As the temperature is raised, the time of lag diminishes in the drop method, until eventually a point is reached where the mixture again fails to ignite spontaneously. This temperature is dependent upon the molecular weight of the paraffin, the dimensions of the tube or bulb, and the activity of the oxidising agent present. The experiments also show the futility of attempting to compare the activities of pro-knock and anti-knock reagents by their effects on ignition temperature and even on lag by the drop method. When members of each class are present together, they neutralise each other's effect. The rate of change of lag with temperature may possibly furnish further useful information.

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