CXVII.—*Autoxidation during Slow Combustion.*

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THE work carried out during 1925 in this laboratory included a study of fuel detonation from the purely physical side (Callendar and others, R. & M. No. 1013), which led to the conclusion that the onset of detonation at high compression ratios, in the case of liquid fuels, was due to the persistence of nuclear drops or residues of low ignition point, forming a relatively small percentage of the

charge. The remarkable effect of very small quantities of organo-metallic compounds, such as lead tetraethyl and iron or nickel carbonyl, was attributed to the reducing action of the metal, which became concentrated in the nuclear residues, thus delaying their ignition.

A further study of the phenomena of slow combustion from the chemical side (Aeronautical Research Committee, R. & M. No. 1062, 1926; *Engineering*, Feb. 4th, 1927) confirmed these con-clusions by showing that such nuclei in the form of fog and dew always preceded or accompanied the initial stage of oxidation. Analysis of the products of the reaction revealed traces of active oxygen, which became much more marked when the fuel was injected in the form of a fine spray, indicating the formation in the nuclear drops of some explosive organic peroxide, which would naturally account for their simultaneous ignition. The addition of lead tetraethyl to the fuel under these conditions completely changed the course of the reaction, inhibiting the appearance of active oxygen in the products, and raising the temperature of spontaneous ignition of the mixture.

Further experimental evidence has since been obtained in support of these conclusions, which helps to clear up some of the difficulties of the subject, and to answer most of the objections which have been raised against the theory of autoxidation.

EXPERIMENTAL.

Several independent methods have been employed, the most important of which will be referred to for brevity as (*a*) the tube method, (*b*) the bulb method.

(*a*) The tube method has been described fully (Callendar and others, *loc. cit.*) and was devised primarily with the view of identify-ing the products of reactions occurring in a fuel–air mixture when passed through a heated tube at any desired temperature. (*b*) In the bulb method, the mixture was heated in a closed bulb in order to obtain supplementary evidence with regard to the rate of reaction as the temperature was slowly raised. In both (*a*) and (*b*), the apparatus was duplicated and arranged differentially with a pair of tubes or bulbs heated under identical conditions, in order to observe more accurately differences of behaviour between different mixtures and changes induced by the addition of small quantities of oxidising or reducing agents.

(*a*) *The Tube Method.*

Some of the results of this method will be briefly summarised before proceeding to particular cases. The temperature of the

furnace, which was varied from about 150° to 700° as required, could be observed at any time with a platinum thermometer inserted in one of the experimental tubes. The temperature at which any action became observable was usually recorded as the temperature of initial combustion, though the reaction indicated was often quite different from that of complete combustion in a flame. The temperature of inflammation—that at which each mixture caught fire—could also be observed with considerable accuracy. The products of the initial reaction were accompanied by a fine and very persistent fog, which passed through all the reagents without absorption. This tended to confirm the nuclear origin of the reaction, but the products isolated were comparatively stable, familiar substances, such as aldehydes and acids, which were found to have no appreciable effect on detonation in an engine. It was concluded that these were final products of decomposition of some more active and unstable compounds, the search for which resulted in the discovery of the presence of active oxygen, presumably in the form of organic peroxides.

Additional Experiments. Tube Method.—(1) *Oxidation of hexane.* The hot gases from hexane–air mixtures were passed directly into slightly acidified potassium iodide solution, and the liberated iodine was titrated with $N/50$-sodium thiosulphate solution. There was only a very small quantity of " active " oxygen present when the gas mixture passing through the tube was heated longer than 1 minute, especially at higher temperatures. With decreasing times of heating, much larger yields were obtained, especially when the mixture was not completely vaporised but was introduced in the form of a fine spray containing minute drops of liquid. This is illustrated in Fig. 1, the values being calculated for 1 g. of hexane consumed (mixture strength about 12%).

In a further attempt to isolate the peroxides, a condenser made of German silver, through which cold water circulated, was inserted into the exit end of the tube heated in a vertical position. The condensate when concentrated in a vacuum left a gummy residue, which did not detonate on heating, but consisted merely of decomposition products. It would thus appear that the life of the primary peroxides (addition products of the fuel with oxygen molecules) is exceedingly short on account of their thermal instability and reactivity.

Staudinger (*Ber.*, 1925, **58**, 1075), who was unable to isolate primary peroxides, used the term " peroxide " for compounds of known structure and the name " moloxide " when the structure of the primary autoxidation product was not known or when the product could not be isolated. He considered that the moloxides

are very rich in energy and too unstable to permit of isolation. The peroxides he succeeded in isolating were violent explosives; for instance, the small amounts clinging to the walls of the container were often sufficient to shatter the vessel.

Legler (*Ber.*, 1885, **18**, 3343) isolated an organic peroxide, which exploded as violently as benzenediazonium nitrate, from the slow combustion products of ethyl ether in air, by concentrating the liquid obtained by condensation. However, this organic peroxide was of smaller molecular weight than the primary peroxide known to be formed from the oxidation of ether in air.

FIG. 1.

Time of heating.

Rate of passage of gas mixture through tube (litres per hour).
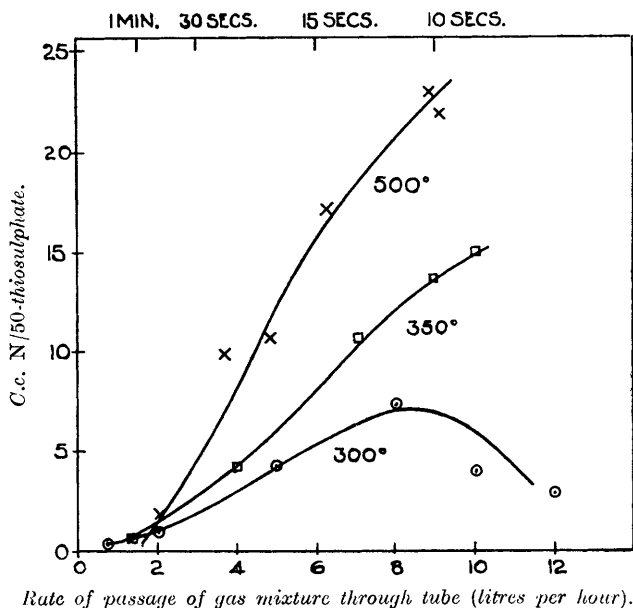
(2) *Autoxidation of benzene, aniline, etc., in presence of hexane.* When a small percentage of alcohol or benzene was added to the hexane, the yield of "active" oxygen was decreased. Other substances had a similar effect, reaching a maximum with iron carbonyl and lead tetraethyl. Some qualitative results are given in Table I for a 15% hexane–air mixture at temperatures below 400° (time of heating, about 25 secs.).

A similar reduction of "active" oxygen was observed when phenol or aniline was added to ether vapour mixed with air.

It was also found that a decrease in yield of aldehydes occurred,

TABLE I.

Substance added to hexane vapour, and approximate proportion.		Effect on amount of " active " oxygen produced.
Ethyl alcohol	5%	Marked decrease.
n-Butyl alcohol	2%	Slight ,,
Benzene and toluene	5%	Moderate ,,
Aniline	2%	Marked ,,
Phenol and m-cresol	—	,, ,,
Carbon monoxide	10%	None observed.
Lead tetraethyl	0·2%	,, ,,
Iron carbonyl	0·1%	,, ,,

especially with iron carbonyl and lead tetraethyl, indicating that peroxide and aldehyde formation were related. These results were obtained with a moderate time of heating and low temperature, no " active " oxygen being detected in the products of combustion of ethyl or butyl alcohol; with more rapid rates of heating and temperatures about 500—600°, a slight amount of " active " oxygen was obtained with ethyl alcohol and a larger amount with butyl alcohol, benzene, etc. (compare Bach, *Compt. rend.*, 1897, **124**, 951).

When benzene vapour was added to a hexane–air mixture and then passed through the hot tube at a temperature below 500° (at which the benzene vapour alone would remain unoxidised in air), autoxidation of the benzene occurred, since when bromine-water was added to the condensed products of slow combustion a small quantity of a white solid separated, m. p. 90°, which was identified as tribromophenol. An experiment was carried out to illustrate the autoxidation of aniline in the presence of hexane undergoing incipient oxidation. Three tubes were placed in the furnace kept at 350°, at which temperature aniline is relatively stable to oxidation. Through the first a hexane–air mixture was passed, through the second aniline vapour and air, and through the third a mixture of aniline and hexane vapour with air, the three tubes being arranged so that the conditions were as nearly as possible the same for all. After the mixtures had been passed for about 1 hour, the tube through which aniline and hexane vapour were passed contained a brown deposit on the walls, especially at the exit end of the tube, and the other tubes were nearly clean. The condition of the dirty tube resembled that with aniline vapour–air at a temperature above 500° when oxidation of aniline is known to occur.

The removal of the " active " oxygen by aniline through autoxidation accounts at once for the anti-detonating action of this substance, but is not in agreement with the primary dehydrogenation theory of Lewis (J., 1927, 1555).

(3) *The influence of hydrogen peroxide on the combustion of hydrocarbons.* In the course of engine experiments at the Air Ministry Laboratory, it was found that hydrogen peroxide solution added

to the fuel behaved similarly to water (Table II). When a fine spray of water was injected into a hexane–air mixture passing through a heated glass tube, the temperature at which the aldehydes were first observed was several degrees higher than without the water. No ionisation was observed below 500°. With a concentrated hydrogen peroxide solution (60%) a similar effect was obtained, and again no ionisation could be detected. It is concluded that hydrogen peroxide does not autoxidise the combustion, and that any such effect previously obtained was due to the initial formation of much more active and unstable peroxides which could yield hydrogen peroxide by hydrolysis.

This conclusion accords with that established by the Traube–Hoppe Seyler discussion on the mechanism of autoxidation (*Ber.*, 1879, **12**, 1551; 1883, **16**, 117; 1889, **22**, 2215), *viz.*, that hydrogen peroxide is a relatively passive substance. Furthermore, the presence of hydrogen peroxide in the products of oxidation has long been known (compare Babo, *Jahresber.*, 1864, 135; Schönbein, *J. pr. Chem.*, 1866, 282, 258), and Clover (*J. Amer. Chem. Soc.*, 1922, **44**, 1107) emphasised the fact that hydrogen peroxide was not a primary product in the oxidation of ether, but one of decomposition.

TABLE II.

Effect of peroxides on the highest useful compression ratio (H.U.C.R.) of fuels determined in an E.35 variable-compression engine.

Fuel.	Observed H.U.C.R.
* 60/40 Ether–alcohol mixture	4·9
,, plus 5% (vol.) water	5·4
,, plus 5% (vol.) H_2O_2 solution (40 vol.)	5·2
Petrol mixture	4·9
,, plus 0·5% (weight) methyl ethyl ketone peroxide ...	4·2
,, plus 2·0% (weight) ethyl hydrogen peroxide	4·1

* Ethyl ether 60%, ethyl alcohol 40% (by vol.).

TABLE III.

The influence of hydrogen peroxide on temperature of ignition (liquid sprayed into tube).

Fuel.	Temp.
(*a*) Ethyl alcohol alone	570°
,, plus 10% (vol.) addition of water	575
,, plus 10% (vol.) H_2O_2 solution (60%)	570
(*b*) *n*-Butyl alcohol...	545
,, plus 10% (vol.) water	559
,, plus 10% (vol.) H_2O_2 solution	560

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Action of Organic Peroxides on the Self-ignition Temperature of Small Drops.

It was shown (Callendar, 1927) that the addition of lead tetraethyl to the spray of a hydrocarbon in air passing through a hot tube extinguished the flashes of flame, and that the addition of a detonation-inducing substance, such as *iso*amyl nitrite, lowered the self-ignition temperature.

Ormandy and Craven (*J. Inst. Pet. Tech.*, 1924, **10**, 335) found that lead tetraethyl apparently had little effect on the self-ignition temperature of petrol drops in the Moore apparatus, but further investigations relating to the self-ignition temperatures of organic vapours, and the effect of numerous anti-knock substances on these temperatures, have been carried out by a number of workers using the Moore method (Egerton and Gates, Aeronautical Research Committee, R. & M. No. 1079; *J. Inst. Pet. Tech.*, 1927, **13**, 244; Weerman, *ibid.*, p. 300; Tanaka and Nagai, *Proc. Imp. Acad. Tokio*, 1926, **2**, 221), and it has been found that lead tetraethyl and other organometallic compounds which delay detonation in the internal-combustion engine have a marked action in raising the self-ignition temperature.

The action of nitrogen peroxide, *iso*amyl nitrite, and benzoyl peroxide on the self-ignition temperatures of sprays of various substances in air passing through a hot glass tube was studied. The results of a number of experiments are in Table IV, from which it will be seen that nitrogen peroxide is particularly effective, and benzoyl peroxide much less so.

Referring to Table IV(*a*), it was found by an additional experiment that, after the temperature of ignition of the butyl alcohol had been *lowered* to 235° by the addition of 5% (by vol.) of nitrogen peroxide, it could be *raised* to 460° by the addition of 5% (by vol.) of lead tetraethyl. At this temperature the mixture burned with a feeble flame, easily extinguished.

The remarkable lowering of the temperature of inflammation of butyl alcohol from 590° to 235° by the addition of 5% of nitrogen peroxide, and the observed violent explosiveness of the mixture, cannot be attributed directly to the liberation of molecular oxygen by the nitrogen peroxide or to its explosiveness, since nitrogen peroxide does not detonate on heating. It is concluded that the effect is due to autoxidation, and that this also accounts for the promotion of detonation in an engine by amyl nitrite and the unstable organic peroxides (Table II).

The theory of autoxidation of fuels in connexion with detonation in the internal-combustion engine has been discussed by Callendar (1927) and the view that peroxidation occurs in the liquid state has

TABLE IV.

Influence of some peroxides and amyl nitrite on spontaneous ignition temperatures.

(a) Nitrogen peroxide, proportion added, % by vol.	n-Butyl alcohol.	m-Xylene.
0	590°	635°
2·5	355	430
5	235	—

(b) Benzoyl peroxide, proportion added, % by weight.	n·Butyl alcohol.	Ethyl alcohol.	m-Xylene.
0	585°	570°	629°
About 2	560	547	613

(c) isoAmyl nitrite, proportion added, % by vol.	n-Butyl alcohol.	m-Xylene.
0	590°	635°
2	552	567
5	545	535
10	518	507
20	455	—

been confirmed by Moureu, Dufraisse, and Chaux (*Compt. rend.*, 1927, **184**, 29), using a different experimental method. It has been demonstrated that the presence of liquid droplets in a gaseous mixture considerably lowers the self-ignition temperature (Bennett and Mardles, J., 1927, 3155; Egerton and Gates, *loc. cit.*).

Callendar (1925) showed that lead particles from the thermal decomposition of lead tetraethyl became concentrated on the surface of nuclear drops, which are thus protected against rapid oxidation and early self-ignition, the primary higher oxides formed by the oxygen molecule with the fuel being immediately decomposed by the metal, and autoxidation being thus delayed.

Egerton and Gates, in order to determine the effect of the metal constituent of dopes, carried out experiments with metal vapours from low-tension arcs, and found that lead vapour behaved similarly to lead tetraethyl in raising the ignition temperature of petrol and in delaying detonation in the internal-combustion engine, a result which is strong evidence for the conclusion that the efficacy of lead tetraethyl is due to the metallic lead formed by thermal decomposition. A similar conclusion has been reached by other investigators from other points of view (*e.g.*, Charch, Mack, and Boord, *Ind. Eng. Chem.*, 1926, **8**, 334; Sims and Mardles, *Trans. Faraday Soc.*, 1926, **22**, 363).

Egerton and Gates have advanced the view that aldehydes, which they regard as having been produced in accord with the well-known hydroxylation theory of combustion of hydrocarbons, form peroxides, which autocatalyse the combustion, giving rise to detonation. This view cannot be maintained in the light of engine

experiments which show that aldehydes do not increase but rather delay detonation.   This result was one of the principal reasons for the replacement of the hydroxylation theory by the autoxidation theory of combustion, the hydroxyl compound which preceded the aldehyde formation, according to the hydroxylation theory, being also a substance not liable to detonate.

FIG. 2.
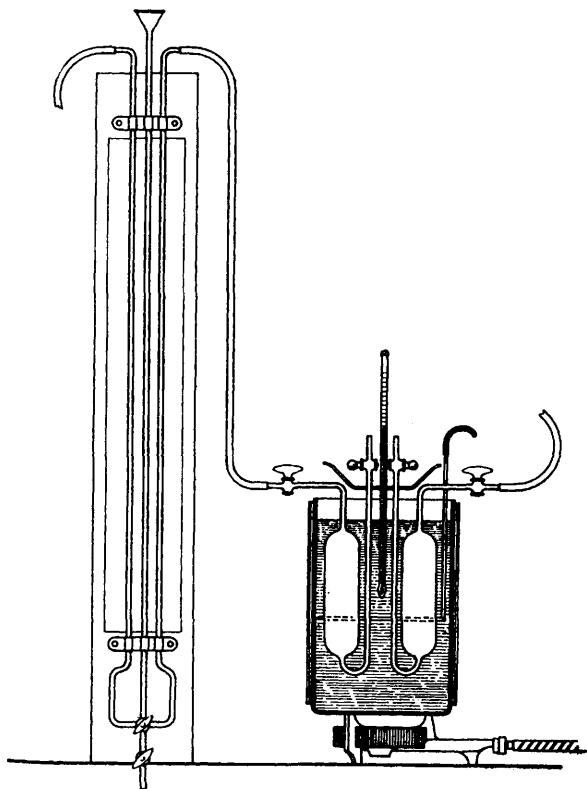
(b) *Initial Combustion of Hydrocarbon–Air Mixtures.   Bulb Method.*

The bulb method has already been described briefly.   The arrangement of the apparatus is shown by Fig. 2.   Two similar bulbs, which can be heated equally in a well-stirred oil-bath, are connected differentially to a toluene manometer, as in Callendar's compensated gas-thermometer; one is filled with dry air and the other with the hydrocarbon–air mixture under test.   The increase of pressure due to heating is balanced by the differential arrangement, and the toluene manometer measures the pressure increase

due to combustion only. This differential method is about 100 times more sensitive than the single-bulb method in general use, in which a *mercury* manometer is used to measure the *sum* of the increases of pressure due to (1) heating and (2) the augmented number of molecules in the mixture due to the chemical reaction. An essential feature of the new design is the provision of tubes and taps at both ends of the bulbs, which greatly facilitate cleaning and drying, and make it easy to fill either bulb at any time with definite mixtures of known strength.

FIG. 3.
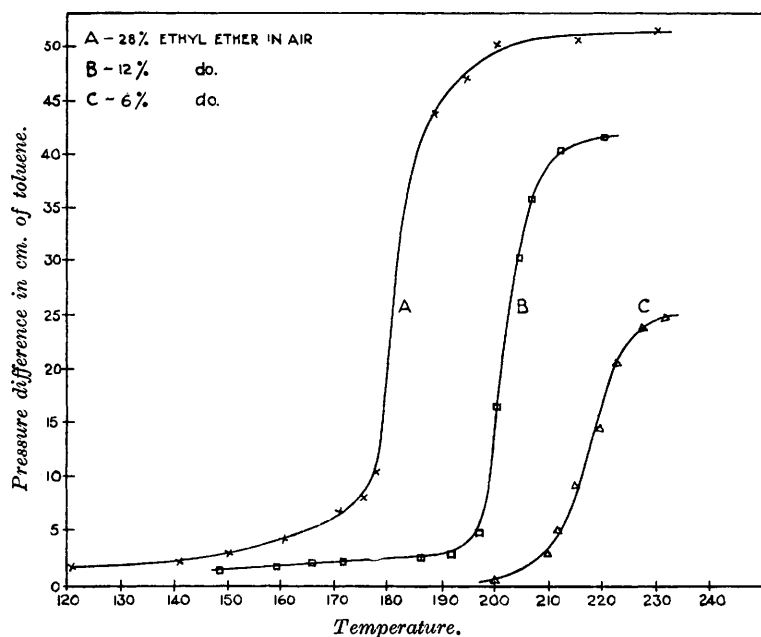
Description of Curves obtained by Bulb Method.—In the interpretation of these curves it must be borne in mind that, whereas in the tube method a continuous flow of mixture is exposed to a very rapid rise of temperature for a short time rarely exceeding 1 minute, in the bulb method a constant volume of mixture is continuously exposed to a slow rise of temperature until the reaction is complete. A few typical curves illustrating the results thus obtained are shown in Figs. 3, 4, and 5. Those in Fig. 3 illustrate the case of simple ether–air mixtures of different strengths, and completely confirm the results of the tube method. The curves are of the usual sigmoid type, and show that the reaction starts very slowly at first,

but that the rate increases exponentially with rise of temperature, becoming very rapid at a fairly definite temperature, and slowing down again as the reaction approaches completion. When the mixture strength is *reduced*, the curve is shifted in the direction of higher temperature by nearly 20° each time the strength is halved, as shown by the curves B and C. This indicates that the reaction is not merely a question of temperature, and that the starting point cannot be stated definitely within 1° or 2° (Lewis, J., 1927, 1560). It further supports the conclusion drawn from the tube method, that the reaction is due primarily to the formation of some very

FIG. 4.
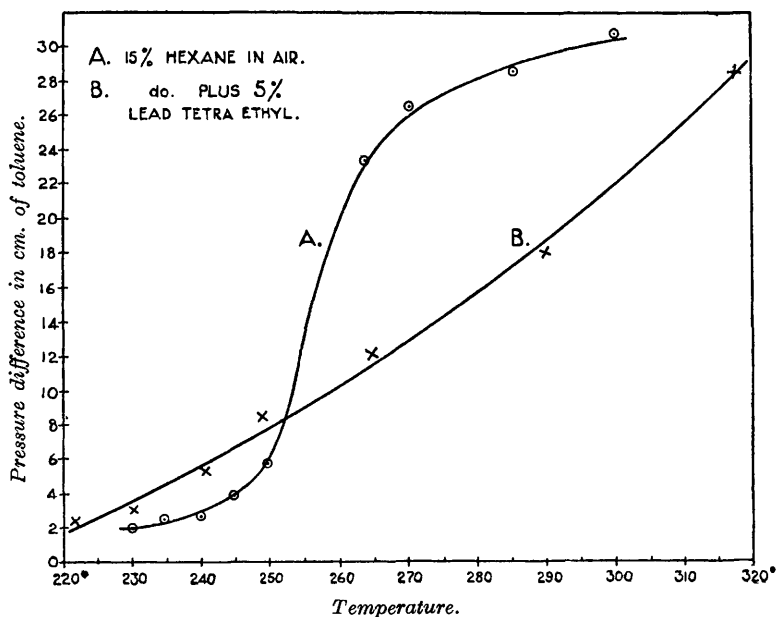
active and short-lived additive compound, probably a peroxide, indications of which were found in the products. Since it has been shown that a reaction of this type occurs most readily in the liquid phase, the effect of mixture strength in lowering the temperature of initial combustion is immediately explained on the nuclear theory by the observation that nuclear drops are formed more readily in strong mixtures than in weak.

The curves shown in Fig. 4 illustrate the effect of adding 5% of lead tetraethyl to a 15% hexane–air mixture. The hexane–air mixture by itself gives a curve A very similar to those in Fig. 3, except that the reaction starts at a higher temperature and is less

rapidly completed than in the case of ether. The effect of a 5% addition of lead tetraethyl is shown by curve B, which appears simpler at first sight but is in reality more complex owing to the presence of three primary components of the reaction; this curve has been corrected (by a separate experiment) for the effect of the decomposition of the lead tetraethyl when mixed with air in the absence of hexane. It has already been shown by the tube method that the first effect of this addition to a hexane–air mixture is to lower the temperature at which the reaction starts, owing to action at the surface of the liberated metal. This effect is confirmed by

Fig. 5.

A *Ether–air mixture plus 5% lead tetraethyl.*
B *Ether–air mixture alone.*
C *Curve " A " corrected for pressure rise due to oxidation of lead tetraethyl alone.*
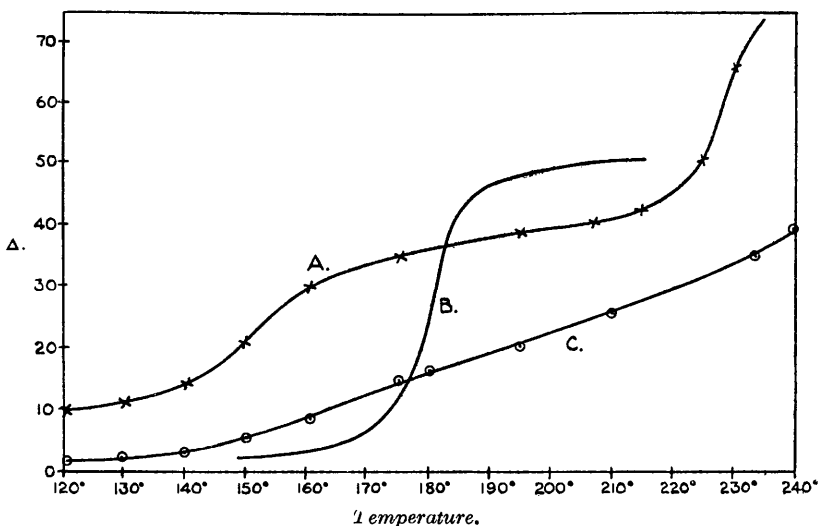
the bulb method. The subsequent course of the reaction is completely modified by the suppression of active oxygen (as demonstrated by the tube experiments) which wipes out the steep rise of the hexane curve A, attributed to autoxidation, by preventing the accumulation of peroxides in sufficient quantity to autocatalyse the reaction.

It is clear that the formation of short-lived peroxides could not be expected to cause any appreciable drop of pressure in the initial stages of the reaction, because any such effect would be more than compensated by their rapid decomposition.

The curves in Fig. 5 (in which the pressure scale is half that of

Figs. 3 and 4) show the effect of lead tetraethyl on a rich ether–air mixture similar to A in Fig. 3. It has already been shown (Callendar and others, R. & M. 1013 ; *Engineering*, April 9th, 1926, *et seq.*) that the presence of ether induces oxidation and decomposition of the lead compound at much lower temperatures than the presence of hexane. This is confirmed by the first part of curve A in Fig. 5, where the increase of pressure shown is due almost entirely to this cause. The corrected curve C, in which this effect is allowed for, is very similar to that found in the case of hexane. Sufficient lead remains, presumably in the nuclei where it would naturally be concentrated, to obliterate the autoxidation stage of the ether curve B at the normal temperature of 180°. But a much larger proportion of lead tetraethyl is required to produce this effect in the bulb method than to prevent detonation in an engine, since it is not merely a question of delaying the reaction for a small fraction of a second as in the engine, but of providing sufficient lead to prevent oxidation of the fuel in the bulb at a given temperature when unlimited time is allowed.

Results and Conclusions.

(*a*) The yield of active oxygen obtained during the slow oxidation of fuel–air mixtures is greatly diminished if heating of the mixture is continued longer than is required for the initial formation of the peroxide, showing that the primary peroxides, owing to their great activity, are very short-lived.

(*b*) The activity of the primary peroxides formed in hexane–air or ether–air mixtures is also demonstrated by the autoxidation of benzene and aniline, which occurs readily in the presence of hexane or ether but cannot be induced at equally low temperatures in their absence.

(*c*) The effects mentioned have been attributed by others to the action of hydrogen peroxide, but the experiments now described lead to the conclusion that the hydrogen peroxide produced from combustion in the heated tube or in the engine during compression is a decomposition product arising from much more active and unstable peroxides previously formed.

(*d*) The experimental work confirms the view (R. & M. 1062) that detonation in an engine using liquid fuel is due to the formation of organic peroxides, which become concentrated in the nuclear drops during compression and ignite them simultaneously when the detonation temperature of the peroxide is reached. The addition of detonation-inducers (such as nitrogen peroxide, amyl nitrite, and benzoyl peroxide) to a variety of fuels shows that the temperature of spontaneous ignition is lowered in all cases, and

detonation-preventers (such as certain organo-metallic compounds) have the opposite effect.

Acknowledgment is made to Professor H. L. Callendar, F.R.S., for his inspiring help, especially with regard to suitable methods and interpretation of the experimental results.

Publication is by permission of the Director of Scientific Research, Air Ministry, London.