PHOSPHORESCENCE AND AUTOCATALYSIS DURING SLOW COMBUSTION.*

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Received 31*st* *August*, 1928.

One of the first manifestations of chemical change in many combustible gaseous mixtures on heating is a faint luminous glow or phosphorescence

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* Investigations made at the Air Ministry Laboratory, Imperial College of Science and Technology, and published by permission of the Director of Scientific Research, Air Ministry.

which, unlike a true flame, does not possess sharp boundaries but extends in the form of a cloud throughout the heated gas mixture. This phosphorescence was observed by Sir Humphry Davy with ether vapour in the neighbourhood of a hot platinum wire and later, in 1882, by Sir William Perkin,[1] with the vapour of organic substances at the surface of a copper sphere. Carbon bisulphide vapour phosphoresces at a low temperature and it has been studied in detail by Professor H. B. Dixon,[2] especially with regard to the extinguishing action of ethylene, coal gas, etc., on the glow. There is an interesting comparison between the extinction of phosphorescence by inhibitors and the action of lead tetra-ethyl in raising the self-ignition temperature of gaseous mixtures whilst in both cases there is an initial suppression of chemical change, indicating the similarity of the mechanism of inhibition. A similar comparison was pointed out a century ago by Thomas Graham[3] between the suppression of the glow of phosphorus and of the inflammability of hydrogen and oxygen mixtures by the presence of certain vapours such as that of ether or turpentine oil.

Recent researches on the problem of detonation in the internal combustion engine have revealed that the "knocking" characteristics of a fuel are closely associated with the formation of highly unstable but reactive organic peroxides at the surface of nuclear particles during the period of slow combustion, and the action of lead tetraethyl in delaying detonation is apparently to inhibit the formation of these primarily formed addition products of fuel and oxygen molecules, moloxides or primary peroxides.[4] The presence of "active" oxygen, presumably in the form of peroxides, has been shown in the products of slow combustion of hydrogen, coal gas, methane, ethylene, ether, petrol, hexane, etc., but the addition of the vapour of "anti-knockers" diminishes or stops the formation of "active" oxygen.

Autoxidation of benzene to phenol occurs when benzene vapour is admitted to a hexane-air mixture undergoing slow combustion, indicating the formation of organic peroxides from hexane.[5] Similarly, benzene and alcohol vapour, methane, etc., which inhibit phosphorescence are oxidised at relatively low temperatures when added to carbon bisulphide undergoing incipient oxidation in air, suggesting that the primary oxidation product of carbon bisulphide is also an active peroxide which is reduced by the inhibiting substances. This removal of the primary highly reactive peroxides, which catalyse the combustion, accounts at once for the powerful action of mere traces of certain substances in suppressing phosphorescence, raising the self-ignition temperature, delaying detonation and suppressing chemical change. An important feature of inhibitory action is the provision of nuclei at the surface of which oxidation begins. Thus, Lord Rayleigh and Professor H. B. Dixon regard inhibitors of phosphorescence as acting by taking prior possession of the nuclei of molecular aggregates, rendering them resistant to oxidation. Similarly, Professor H. L. Callendar in his nuclear theory of detonation regards the nuclei as centres of ignition; and lead tetra-ethyl, by concentration in the drops decomposes the primary peroxides formed at the surface, thus delaying detonation.

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[1] *J. Chem. Soc.*, **41**, 363.

[2] Dixon and Russell, *J. Chem. Soc.*, 1899, **75**, 600; Dixon, *Rec. Trav. Chim.*, 1925, **44**, 305.

[3] *Pog. Ann. Physik*, 1829, **17**, 375.

[4] Callendar, *Engineering*, 4th Feb., 1927.

[5] Mardles, *J. Chem. Soc.*, 1928, 872.

Experimental Methods.

For observing phosphorescent flames and the presence of fog in gaseous mixtures on heating, the apparatus consisted of a combustion tube about 2 feet in length and 1 inch in diameter round the central 8 inches of which was wound an electric heating coil inserted between mica to secure more uniform heating and protection from draughts. The tube was provided at one end with a glass end plate and a side tube through which the fuel vapour mixtures entered, whilst projecting into the tube from the other end was a thermocouple. Air was supplied to this tube by a pressure drum similar to that described previously,[4] the only addition being that of an adjustable pressure release valve. The air was bubbled through sulphuric acid, passed through tubes containing calcium chloride, soda lime, and cotton wool filters, through a small calibrated orifice (the pressure difference across which was measured by a water manometer) into a special form of wick carburettor where it was charged with the vapour required. The wick had the effect of providing an evaporation surface at constant level, enabling mixture strengths to be maintained constant to the degree of accuracy required. The metals employed for the thermo-couple were platinum and platinum-rhodium; the junction was enclosed in glass in order to avoid the possibility of catalytic action. The couple was calibrated against a platinum resistance thermometer, reading on a Whipple indicator; a Callendar nickel heater being employed for the purpose. For the observations on fog formation, a parallel beam of light was passed down the glass tube and a movable mirror was arranged so that when required the source of illumination (pointolite, arc or quartz mercury vapour lamp) could be changed immediately; and the fogs were viewed by scattered light, in a direction perpendicular to the parallel beam. Observations of the chemical changes were made in glass tubes and bulbs by methods already described,[5] the stream of gases passing through the tubes at approximately the same rate as in the experiments for phosphorescence and fog formation. The glass bulbs of about 200 c.c. capacity, one filled with dry air and the other with the gas mixture under test, were connected differentially to a toluene manometer such as in Callendar's compensated gas thermometer. The increase of pressure due to heating was balanced by the differential arrangement so that the toluene manometer measured the pressure increase due to chemical change.

The mixture strengths referred to in the paper are expressed as percentages of the vapour or gas by weight in air. For sake of convenience the experimental results have been divided into 4 parts, *viz.*: Results with (*a*) carbon bisulphide, (*b*) ethyl ether, (*c*) acetaldehyde and amylene, (*d*) hexane.

(*a*) Experimental Results with Carbon Bisulphide.

When a carbon bisulphide-air mixture 19 per cent. rich, was passed through the glass tube used for observing fog formation and the temperature slowly raised the first sign of change was the appearance of a few wisps of very fine blue haze just discernible with care below 100° C. As the temperature approached 150°, the fog which had hitherto remained very thin began to increase and a very faint phosphorescence, visible only with special care, appeared. With further increase in temperature the light beam in the fog test became brighter, the phosphorescence became stronger and more extended whilst sulphur dioxide could be detected at about 175°. At 195° there was a strong explosion with a lilac coloured flame, followed by an intense fog and copious evolution of sulphur dioxide. These combustion changes were followed also by means of the differential bulb apparatus.

The first signs of chemical change were noted about 100° C., corresponding to the fog formation, by a small difference in pressure which slowly increased until about 145° was reached when acceleration of the changes occurred corresponding to the beginning of luminescence and formation of pronounced fog. It will be seen from Fig. 1 that the changes occur at a lower temperature with the leaner mixture, a behaviour contrary to that observed with ether and hexane, etc., the curves relating the temperature of initial combustion, T.I.C. (*i.e.*, when it is possible first to detect sulphur dioxide, aldehydes, and other oxidation products), with mixture strength being smooth U-shaped curves. The relation between mixture strength and T.I.C. is of some interest, since it is not in accord with the law of mass action. It supports the view that nuclear particles are formed prior to oxidation, these particles, probably ionised, forming the centres of chemical change.

TEMPERATURES OF INITIAL COMBUSTION OF HEXANE, ACETALDEHYDE, ETHYL ETHER AND AMYLENE COMPARED WITH THOSE OF CARBON BISULPHIDE

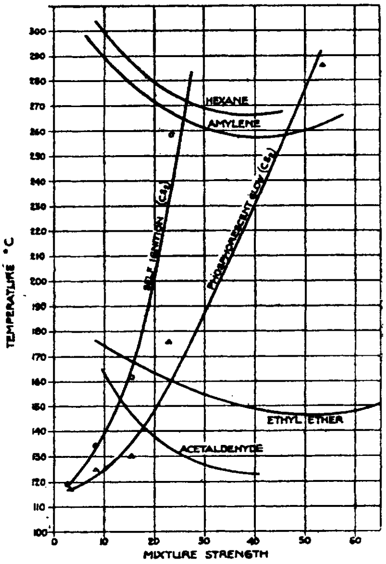

FIG. I.

With carbon bisulphide-air mixtures it was found that with the leaner mixtures self-ignition occurred from 119° upwards, whilst with the richer mixtures inflammation was delayed and slow combustion with phosphorescence occurred as first described by Turpin, 1890.[6] He stated that a stream of air passing over liquid carbon bisulphide could be sent through a glass tube heated to 200° where it glowed without bursting into flame, depositing a red-brown volatile solid on the glass with the formation of sulphur dioxide.

Differences in the character of inflammation were noted, and these appeared to depend on the presence of slow combustion products, because a lower ignition temperature was obtained when the gas mixture was passed suddenly into a hot tube than that found when the tube was gradually heated whilst the gas mixture was passing. This behaviour is in accord with the statement of Dixon[2] that if the gas mixture failed to ignite in his concentric tube the power of inflammation was restored by a prolonged sweeping out of the cylinder, which suggested that some product of combustion remained and inhibited ignition.

The anomalous behaviour of carbon bisulphide-air mixtures in that the richer mixtures appear to be more stable against oxidation, contrary to the general behaviour of hexane, hydrogen, coal-gas, etc., in air, calls for some comment. The excess carbon bisulphide appears to behave

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[6] *Brit. Assoc. Report*, 189 , p. 776.

as its own inhibitor. This would follow quite naturally if there is interaction between a carbon bisulphide molecule and its primarily formed peroxide, for example as in the following equation :—

$$CS_2/O_2 + CS_2 \rightarrow CS_2 + CS + SO_2,$$

whereby the catalyst CS_2O_2 is removed and combustion suppressed.

A similar behaviour probably occurs to a smaller extent with other gaseous mixtures including carbon monoxide and hydrogen, and this effect must play an important part in the mechanism of combustion and the tendency of a fuel to detonate in the engine.

Fog and Phosphorescence Experiments with Carbon Bisulphide.—The fogs extended throughout the whole length of the tube and were blue. This suggested that they were composed chiefly of solid, rather than liquid particles. The method of experiment was to switch out all lights as soon as fog appeared, and to continue heating. Immediately the phosphorescent glow commenced, the temperature was observed, the heating then being continued in darkness until the vapour reached the temperature at which ordinary combustion occurred.

As the temperature increased the glow, at first very faint, became brighter and more extended, until eventually it appeared to divide and a slow moving blue flame or a rapid explosive flame, according to mixture strengths, passed along the tube. The temperature at which this occurred is referred to in the table below as the "ignition temperature," although actually there appears to be continuous transition from the state of phosphorescent combustion to ignition as ordinarily understood.

The glow appeared always at a temperature above that at which fog was first observed; in the case of weak mixtures only slightly above. Mixture strengths ranging from 4 per cent. to 50 per cent. were employed, and over the range 4 per cent. to 20 per cent. the temperature of fog formation was in the neighbourhood of 100° C. With the very rich mixture however, this temperature rose to 240° C. The temperature at which the glow appeared and inflammation occurred, increased with increase of mixture strength, at first slowly, and later quite rapidly; these observations being in accord with the view that in very rich mixtures, the excess carbon bisulphide acts as its own inhibitor.

TABLE I.—EFFECT OF MIXTURE STRENGTH ON RESULTS WITH CARBON BISULPHIDE.

Mixture Strength (by Weight).	Initial Fog Temp. (° C.).	Initial Glow Temp. (° C.).	Ignition Temp. (° C.).	Nature of Ignition.
4·5	112	119	119	Cool slow moving blue flame.
8·9	124	126	130-140	Faster vivid blue flame; quiet burning.
16·1	110	130	162	Fast but quiet flame of greater brilliance.
23·0	97	177	259	Brilliant flame; mildly explosive.
54·0	240	288	355	Less brilliant flame; less explosive and redder colour.

With the 54 per cent. mixture the inflammation was accompanied by copious deposition of a white solid, presumably white sulphur.

Action of Inhibitors.—Using a carbon bisulphide mixture of 4 per cent. which gave a steady glow at 200°, the effect of many substances was investigated. Benzene vapour had a marked effect, no fog, glow or sulphur dioxide being observed until a temperature of 350° was reached. Bromine, amyl nitrite and ethyl nitrate behaved similarly to benzene; it was necessary to heat the tube, after removal of the nitrite to a temperature of nearly 400° C., before the glow could be induced to reappear, whilst after using ethyl nitrate or bromide, no glow could be obtained until the tube was taken down and cleaned. Iodine was less effective than bromide. Pentane vapour quickly extinguished the glow, as did acetaldehyde, ethyl acetate, ethylene dibromide, and pyridene in order of decreasing efficacy. Acetone and acetic acid both inhibited the glow completely after a few minutes, but did not appear to be very powerful. Chloroform vapour and ammonia reduced the intensity of the glow considerably but did not extinguish it unless added in excess. Methyl and ethyl alcohols suppressed the glow completely. Ethyl ether vapour had the same effect as iron carbonyl; the glow was reduced in intensity, and became less concentrated; after a little time this diffuse glow weakened still further, then began to fluctuate both in position and intensity, and finally passed quickly into separate combustion waves (blue flames) along the tube. With lead tetra-ethyl the glow at 200° was extinguished. At 400° C., with the same amount of lead tetra-ethyl, the glow became only slightly less intense and more diffuse. Aniline and phenol were found to have little or no effect on the glow at 200°. The four gases, acetylene, coal gas, ethylene, and sulphuretted hydrogen, all extinguished the glow completely and with about equal rapidity but the glow reappeared a few minutes after the gas had been shut off. The only substance found whose effect was the reverse of inhibitory was carbon monoxide. The glow was intensified considerably and extended in the presence of this gas. This result being in contradiction to that recorded by Dixon,[2] the experiment was carefully repeated and confirmed. The effect of copper on the glow at 200° C. was investigated by inserting a small piece of copper gauze, which almost filled the tube's cross-section. The intensity of the glow appeared to remain unaffected, but it became concentrated on the surface of the gauze.

The following experiments were carried out by the tube method to investigate the action of inhibitors and the presence of metals on the slow combustion of carbon bisulphide-air mixtures. When *iso*-pentane, a powerful inhibitor, was added to a 22 per cent. carbon bisulphide-air mixture the slow combustion of the carbon bisulphide was delayed until the T.I.C. of *iso*-pentane (*viz.*: 300°) was reached. By means of a companion tube through which the same *iso*-pentane mixture alone in air was being passed, it was found that the degree of oxidation of pentane was about the same in both tubes over the temperature range 300°-400°.

Other organic substances tried in the phosphorescence experiments were used. With all of these the slow combustion was delayed. The self-ignition temperature was also considerably raised. Typical results are given in Table II.

The effect of *iso*-amyl nitrite and ethyl nitrate vapour on the combustion behaviour of a 5 per cent. carbon bisulphide mixture which ignited with some violence at 159° was tried. The addition of about an equal amount of *iso*-amyl nitrite raised the self-ignition point to 245° which was found to be nearly the same for the *iso*-amyl nitrite mixture when taken alone, *viz.*, 250°. Below this temperature there appeared to be very little change, apart from a fog formation, until 240° was reached when the litmus solution began to be slowly affected. Ethyl nitrate vapour also delayed the self-ignition temperature and the T.I.C.

TABLE II.—THE SUPPRESSION OF OXIDATION IN CARBON BISULPHIDE-AIR MIXTURES.

Mixture.	Temperature when Litmus Solution was first Affected (° C.).
(*a*) 22 per cent. bisulphide in air	190 (Ignition at 320).
(*b*) Mixture *a*, diluted with 15 per cent. acetylene	237 (No self-ignition though temp. raised to 350).
(*c*) Mixture *a*, diluted with 20 per cent. coal gas	400 (No self-ignition though temp. raised to 500).
(*d*) Mixture *a*, diluted with 10 per cent. ethylene	380 (No self-ignition though temp. raised to 450).
(*e*) Mixture *a*, diluted with 30 per cent. carbon monoxide	310
(*f*) Mixture *a*, diluted with 10 per cent. benzene vapour	350
(*g*) Mixture *a*, diluted with 7·5 per cent. ethyl alcohol vapour	340
(*h*) Mixture *a*, diluted with 15 per cent. ethyl ether vapour	280 (Fog at 180 but no ignition below 450).
(*i*) Mixture *a*, diluted with 10 per cent. aniline	(Ignition at 350).

Action of Lead Tetra-Ethyl, Iron Carbonyl, Metals, etc.—When a few fragments of iodine were added to the warm tube, the gas mixture apparently remained unchanged even though the temperature was raised to 400°. A 4 per cent. carbon bisulphide mixture in air exploded loudly at 163° but when the air supply was first bubbled through iron carbonyl the first sign of change was at 180° when a fine blue fog appeared, although the presence of sulphur dioxide could not be detected. At 245° there was a yellow flash of light followed by a copious evolution of sulphur dioxide. Repeating the experiment with lead tetra ethyl a similar result was obtained, quiet inflammation occurring at 343°. Some strips of copper gauze were rolled and inserted into the combustion tube—the mixture which exploded at 165° now remained unchanged until 177° was reached when a small amount of sulphur dioxide was evolved. At 375° the mixture ignited. The copper gauze during the experiment had become slightly darker but no marked change had occurred. A number of other metals were tried and the results are shown in Table III. :—

TABLE III.—ACTION OF METALS ON THE OXIDATION OF CS_2 VAPOUR.

Metal.	Temp. when slow Combustion began, noted by Change in Litmus Solution (° C.).	Self-Ignition Temp. (° C.).
None	155	163
Copper gauze	177	375
Lead foil	180	205
Iron filings sprinkled on bottom of tube .	180	185
Zinc (granular)	280	above 400
Tin ,, ...	about 250	340
Aluminium turnings	320	350
Nickel foil	200	375
Small piece of platinum foil . . .	180	210
Bismuth	330	335
Magnesium ribbon	270	307

The remarkable extinguishing action of ethylene on the inflammation of carbon bisulphide mixtures was apparently first discovered by Frankland[7] who was investigating the cause of a street coal gas explosion. Later, in 1890, Turpin[6] showed that sulphur dioxide raised the self-ignition temperature from 160° to 260°. Dixon[2] has investigated the action of hydrogen, carbon dioxide, etc., on the self-ignition temperature and phosphorescence, and found that whilst some substances were relatively inert others were noxious or poisonous even in traces. White[8] who investigated the lower limit of combustion of carbon bisulphide mixtures found that it was specifically catalysed by some product of oxidation.

The Mechanism of Inhibition.—A number of chemical experiments were undertaken to investigate the possible mechanism of inhibition which would account at once for the inhibition of phosphorescence, of self-ignition and the delaying of the slow combustion observed. When the following substances were vaporised and mixed with air the temperatures of initial oxidation changes were observed to be: coal gas 590°, ethylene 453°, benzene 660°, ethyl alcohol (aldehyde formation) 425°. Although benzene was thus found to be very stable to oxidation by air yet when added to a carbon bisulphide mixture and passed through a hot tube at about 400°, the benzene was oxidised to phenol; the addition of bromine water to the water through which the exit gases had bubbled, precipitated the bromophenols. Similarly when coal gas, ethylene or ethyl alcohol was addded to a carbon bisulphide mixture at a temperature below their respective T.I.C.'s and during the slow combustion of the carbon bisulphide autoxidation occurred in all the cases as indicated by the formation of aldehydes. The autoxidation of benzene, coal gas, ethylene, and ethyl alcohol during the slow combustion of carbon bisulphide in air can be accounted for by the formation of a peroxide. This primary peroxide (CS_2O_2) is probably the catalyst of combustion and its destruction during the autoxidation of benzene, alcohol, ethylene, etc., accounts at once for the inhibition of chemical change and consequently of phosphorescence and self-ignition.

Dixon attempted to explain the inhibition phenomenon by suggesting that the carbon monosulphide or its molecular aggregation with carbon bisulphide is responsible for phosphorescence. He considered that ethylene and other inhibitory molecules fastened or condensed on the nucleus poisoning it against further oxidation at an early stage. This view of the function of carbon monosulphide has been criticised by White[8] from the results of experiments on the spontaneous ignition of sulphur in the presence of inhibitors.

Experimental Results with Ethyl Ether.

A highly explosive peroxide has been isolated from the products of slow combustion of ethyl ether by Legler.[9] The formation of reactive peroxides is also indicated by the autoxidation of benzene in the presence of ether undergoing slow combustion in air at a temperature when benzene vapour alone in air remained unoxidised. When pure ether vapour in air was passed through glass tubes which were gradually heated, the T.I.C. was noted by the deposition of dew on the cold sides of the tube at the exit end and by the test for aldehydes. The temperatures given in Table IV. were found with different mixture strengths :—

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[7] *Chem. News*, 5, 3, 1862.

[8] *J. Chem. Soc.*, 1927, 793.

[9] *Ber.*, 1885, 18, 3343.

TABLE IV.

Mixture strength	8·3	22	28	45	49	55	65
Temp. initial combustion (° C.) .	175	165	159	147	146	145	147

Iron carbonyl was found to influence the combustion of ether in air to a greater extent than lead tetra ethyl, the amount of active oxygen present in the products of slow combustion being reduced to a greater extent by the iron compound. With a mixture of ether in air (8·3 per cent.) which had a T.I.C. of 170°, the effect of iron carbonyl and lead tetra-ethyl was to *lower* the T.I.C. to 140° and 145° respectively. A similar result was obtained when metals were introduced into the combustion space. Iron turnings had a greater effect than lead foil. Copper and bronze turnings had a marked effect in inhibiting peroxide formation but were less effective than zinc and tin in delaying the formation of carbon dioxide. Magnesium and aluminium caused only slight changes in the combustion.

The quantitative results obtained by chemical analysis of the products of combustion are shown in Table V. The aldehydes were calculated as acetaldehyde: the acids as acetic acid.

TABLE V.—COMBUSTION OF ETHER IN AIR.

Temp. (° C.) . .	145			200			320			450		
Mixture strength (°/₀)	35	15	15*	35	15	15*	35	15	15*	35	15	15*
Aldehydes . . .	3·7	7·5	1·7	46·5	—	39	37	47	30	22	35	15
Acids . . .	0·8	1·2	0·2	21	—	12	15·5	22·5	3·7	5	9	1·5
CO_2	0·5	1·2	0·5	3·5	—	2·1	10·5	14·5	7·5	29	25	30
CO		—			—		24	—	16·5	27	—	—

Fog and Phosphorescence.—On slowly heating an ether vapour-air mixture of strength about 5 per cent., the following changes were observed with regard to fog formation. Between 30° and 50° a very faint wisp of fog appeared which, however, disappeared on slight further heating. At about 180°, a thin fog would again appear in the cooler portions of the experimental tube. In the hotter portion of the tube, the particles were probably too small to be observed. The fogs became more intense on further heating and particle motion was always visible. With light from a pointolite lamp, the fog appeared quite blue in colour at first, when viewed perpendicularly to the beam. As the temperature was increased and the fog became thicker, its colour became whiter. Observed obliquely to the tube, these fogs showed brilliant bands of colour, which repeated themselves in definite orders along the length of the tube. Decided thickening of the fogs occurred near 190° C., and the tube temperature was observed to rise sometimes as much as 15°. At about 220° C. "combustion waves" commenced; these took the form of blue flames visible in a darkened room. On further heating, the flames became more frequent, until finally at about 240° continuous combustion commenced with a steady blue phosphorescent flame. This flame was quite distinct from an ordinary hot flame. With the passing of the first combustion wave the already intense fog thickened, and with each wave a momentary rise in temperature of 10° to 15° occurred.

Action of Inhibitors.—The tube temperature was kept at about 250° C. and the mixture strength was 5 per cent. approximately. Benzene had no effect on the glow and lead tetra ethyl caused only a slight diminution in its intensity. Iron carbonyl completely extinguished the glow after causing

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* With iron carbonyl vapour present.

it to pass from the bright flame to the diffuse and weak phosphorescent form. Bromine nearly extinguished the glow, whilst iso amyl nitrite and methyl alcohol both reduced its intensity, but failed to extinguish it completely. Nitrogen peroxide extinguished the glow; a single small "puff" being sufficient for the purpose. When a small amount of nitrogen peroxide was passed continuously into the tube with the ether-air mixture, a fog was obtained at ordinary temperature. This fog persisted up to 500°. No glow was observed: but above 500° a violent explosion occurred. With a richer mixture the glow appeared at just under 400° C.: the brown colour disappeared immediately the glow occurred, and the tube was subsequently heated to 530° C. without explosion.

Ethyl nitrate had no apparent effect on the glow but changed the character of the combustion; the cool blue ether flame was replaced by a bright mauve flame, and the quiet wave gave place to an explosion. The glow with ethyl ether-air mixtures was usually less bright than with carbon bisulphide mixtures, but the glow once established persisted although equal volumes of benzene, alcohol, amyl nitrite vapour, etc. (which with carbon bisulphide act as powerful glow inhibitors) were added. Inhibitors of the phosphorescence of ethyl ether were in every case powerful inhibitors with carbon bisulphide.

It will be seen from the chemical data relating to the products of combustion that iron carbonyl does not have a great effect on the combustion results; this corresponds with the relatively small effect on the phosphorescence. The extinguishing action of nitrogen peroxide and bromine appears to be different from that of oxidisable substances such as organic substances or lead tetra ethyl. Similar instances are quoted by Bäckström [10] who points out that the strong inhibitors might have some specific power of depriving the excited molecules of their energy and dissipating it in some physical manner, *e.g.* in the form of kinetic energy.

Usually it is possible to show that the order of inhibition by substances is directly proportional to the ease of oxidation. In delaying "knocking" in the engine the tertiary amines are less efficacious than the primary or secondary amines, and this can be explained by the fact that the tertiary amines can only be oxidised with the simultaneous destruction of the molecule whereas the primary and secondary amines can be readily oxidised by the simple removal of hydrogen.

(*c*) **Results with Acetaldehyde and Amylene.**

The aldehydes and amylene phosphoresce similarly to ethyl ether when the vapour is heated in air, the phosphorescence being accompanied by polymerisation and chemical changes into formaldehyde, acetic acid, etc. The first change in the gaseous mixtures on heating was indicated by fog formation and the deposition of dew on the cold exit end of the glass tube, the T.I.C. varying considerably with the mixture strength as shown in Fig. 1. Using the closed bulb method it was possible to follow very slight changes which occurred at still lower temperatures when the time of heating was more than twenty fold that in the glass tube experiments (Figs. 2 and 3).

The phosphorescent flames which with a 28·4 per cent. mixture appeared at 257° and in an 8 per cent. mixture at 305° C. passed slowly along the tube and then became extinguished, but at higher temperatures the flame pulses became more frequent and finally settled down to a steady blue glow

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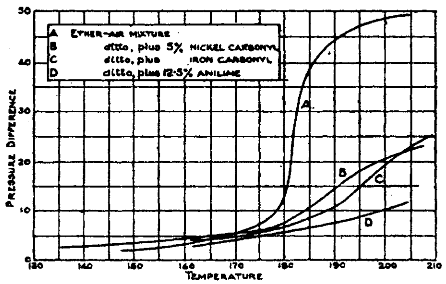
[10] *Med. K. Vat. Nobel Institut*, **6**, 16, 1927.

visible only in complete darkness. With amylene-air mixtures phosphorescence and fog formation appeared to coincide, the temperature being that at which the amylene first showed signs of oxidation.

FIG 2. THE SLOW COMBUSTION OF ETHER IN AIR (CLOSED BULB METHOD) WITH AND WITHOUT INHIBITORS



Action of Inhibitors.—Both iron carbonyl and lead tetra-ethyl exerted a slight influence. The T.I.C. of acetaldehyde and amylene was lowered like that of ethyl ether, but quantitative analysis of the slow combustion products indicated that there was only a slight change in the amount of combustion at moderate temperatures. This behaviour is shown by the curves obtained with the addition of lead tetra-ethyl and iron carbonyl (Figs. 2 and 3), which show that the pressure difference begins at a lower temperature but increases much more slowly with rise of temperature. The chemical data in Table VI. relate to the oxidation of acetaldehyde vapour in air at different temperatures with and without iron carbonyl and lead tetra ethyl.

Methane and the vapour of methyl and ethyl alcohols, phenol and benzene were found to have no effect on the acetaldehyde glow. Ammonia caused it first to contract, then to become fluctuating and finally to disappear. Carbon bisulphide and iodine vapour caused the glow to extend slightly, whilst aniline quickly extinguished the glow. Lead tetra-ethyl had no visible effect on the continuous glow, but when admitted to the intermittent combustion waves their temperature as judged by the momentary rise indicated by the thermocouple was slightly reduced. Iron carbonyl quickly extinguished the glow. A small amount of nitrogen peroxide sufficed to extinguish the glow and to raise slightly the temperature at which fog first appeared. Ethyl nitrate delayed the temperature of fog formation by 20°, but caused combustion waves and continuous glow to set in earlier. Ethylene

THE SLOW COMBUSTION OF ACETALDEHYDE IN AIR (CLOSED BULB METHOD) WITH AND WITHOUT INHIBITORS.

FIG. 3

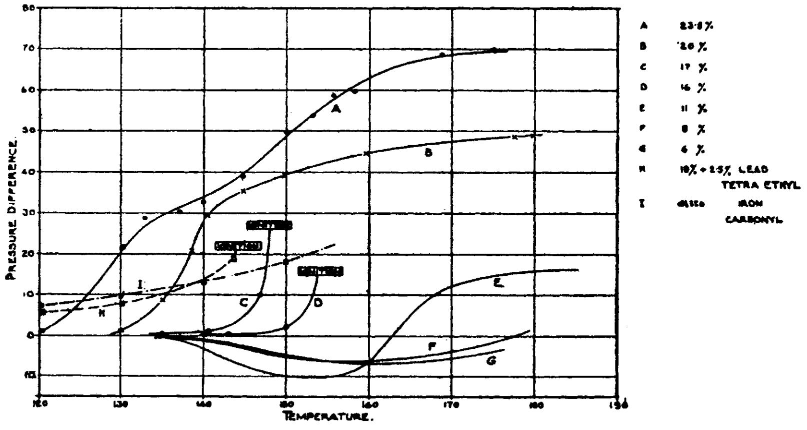


TABLE VI.—SLOW COMBUSTION PRODUCTS OF ACETALDEHYDE.

Temperature (° C.).	Mixture Strength.	Percentage Amounts by Weight.			
		Carbon Dioxide.	Aldehydes.*	Acids.	Carbon Monoxide.
300	20·5	5·5	11	1·0	16
	10·0	10·0	12	0·6	18
400	21·8	7	10	1·4	—
	11·9	14	13	1·0	—
500	16·4	8·7	7·5	0·5	30
	8·4	10·7	14·0	1·2	—
500 †	15·3	12	12·2	1·8	20
500 ‡	6·3	10	7·0	0·5	30

appeared to be without effect, but carbon monoxide was interesting since it caused the glow to contract and become more intense, as in the experiments on carbon bisulphide. In a later experiment, intermittent combustion was in progress when carbon monoxide was passed into the tube. The waves ceased and gave place to a small bright continuous glow, which suggested that carbon monoxide promoted combustion. Iron carbonyl and carbon monoxide appeared to exert little influence on the glow of amylene in air.

The influence of many metals on the combustion was examined by placing metallic foils, etc., in the tube. With copper, silver, gold, and platinum foils, no effect could be observed, but iron, lead, and thallium all promoted combustion at the metallic surface. If the metals were introduced when intermittent combustion was in progress, a surface glow also appeared. Before each wave the continuous glow gradually increased in intensity and finally spread into the flame itself. Immediately the flame had passed, a weak glow again appeared and the process was repeated.

The action of inhibitors on the phosphorescent glow of acetaldehyde and amylene resembled that on the glow of ethyl ether, suggesting that the mechanism of inhibition is the same or similar for all three. It is known that all these substances are capable of forming peroxides of relative stability which have been isolated.

(*d*) Results with (normal) Hexane.

Hexane vapour phosphoresced in air after the formation of a fog which coincided with the oxidation to aldehydes, acids, water, etc. It was desired to know whether the glow was due to the hexane or to the aldehydes formed during oxidation.

Hexane closely resembled acetaldehyde in the definiteness of its fog formation. A 13·7 per cent. mixture gave a thin fog at 308° C. followed by intermittent combustion waves and rapid thickening of the fog at 314°. When combustion began, the temperature rose spontaneously to about 330° and the thermocouple jumped momentarily to 340° with the passage of each blue flame. The complete absence of red and the prevalence of blue colour seemed to indicate that the fog particles in hexane were of small size.

Nitrogen peroxide caused fog to appear at a temperature 50° below the

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* Calculated as acetaldehyde ; this value includes any unchanged acetaldehyde.

† With approximately 0·5 per cent. iron carbon.

‡ With approximately 0·5 per cent. lead tetraethyl.

fog temperature for hexane air alone. It completely prevented the appearance of intermittent combustion waves and continuous glow, but the mixture exploded violently at 430° C. The brown colour disappeared on explosion but returned immediately after. When nitrogen peroxide was admitted to the continuous glow of hexane-air at 350°, the glow disappeared completely.

Ethyl nitrate and carbon bisulphide had no effect on the glow: carbon monoxide caused it to brighten considerably (as with acetaldehyde and carbon bisulphide), whilst ammonia rapidly extinguished the glow. The effect of passing in lead tetra-ethyl with the mixture was to delay the glow from 315° to about 350° and to make the combustion waves much cooler. The "waves" took the form of a faint pulsating glow in the centre of the tube, instead of the intermittent blue flame travelling along it. The action of lead tetra-ethyl on the glow of acetaldehyde was negligible but its effect on the hexane glow was quite marked. Thus when the lead tetra-ethyl was admitted the glow became more diffuse and gradually fainter, and disappeared completely in a few minutes. Iron carbonyl first made the glow feeble and fluctuating, then suppressed it completely. Bromine completely extinguished the glow, as did ethyl alcohol when the air stream was bubbled through the liquid. With a smaller amount of ethyl alcohol, the glow was rendered very faint. Methyl alcohol was less powerful than ethyl. Amyl nitrite, ethyl acetate, ethylene dibromide, and chloroform had the same effect as methyl alcohol, the action of amyl nitrite being quite marked and that of chloroform being much weaker. The hexane glow appeared to be quite unaffected by platinum, gold, silver, copper, aluminium, and tin foils. Thallium, chromium, vanadium pentoxide (used in a porcelain boat) and lead also had little or no effect: and the only apparent effect of an iron strip was to cause the glow to spread over the surface of the iron, the intensity remaining unchanged.

The influence of lead tetra-ethyl, iron carbonyl, aniline, and other inhibitors as well as the action of metals on the chemical changes which occur during the slow combustion of hexane have been already discussed (Callendar, *loc. cit.*). There appears to be a close correlation between the inhibition of phosphorescence and of chemical change.

Summary.

The results of experiments dealing for the greater part with the inhibitory action of certain substances such as lead tetra-ethyl, iron carbonyl, iodine, ethylene, etc., on phosphorescence and chemical change during slow combustion suggest that peroxidation, occurring at the interface of nuclear particles, is directly responsible for phosphorescence, autocatalysis, and for detonation in the internal combustion engine. Inhibitors, by reacting with the primarily formed peroxides, remove their active oxygen and energy and in this manner destroy the positive catalyst of combustion and cause of phosphorescence and detonation. An important feature of the work is the demonstration that benzene, coal gas, alcohol, ethylene, etc., which can inhibit phosphorescence and delay detonation are autoxidised in the presence of carbon bisulphide, hexane, etc., undergoing incipient combustion, and this provides a further proof of the momentary existence of organic peroxides or of CS_2O_2 in the case of carbon bisulphide.

The phosphorescent glow of carbon bisulphide, also self-ignition and slow combustion changes are inhibited by excess of carbon bisulphide. An important point in connection with the mechanism of combustion of hexane is that lead tetra ethyl and ethyl alcohol have a marked action on the glow

and chemical change whereas with acetaldehyde the action is slight. This would seem to indicate that the glow of hexane is not due to the intermediate formation of aldehydes but due specifically to the formation of primary peroxides of hexane.

In experiments carried out by inserting various metals in the combustion tube it was found that the glow usually seemed to be confined to the metal surface which remained unchanged whilst the course of chemical change was altered, there being a considerable decrease in intermediate combustion products and a delay in self-ignition. This inhibitory action of metals is in accord with the view that organo-metallic compounds such as lead tetra ethyl owe their efficacy to the colloidal metal formed by thermal decomposition at the surface of nuclear particles.

Acknowledgment is made to Professor H. L. Callendar, F.R.S., for his inspiring help and supervision.