XI.—*Low-temperature Oxidation. Part II. The Ignition of Some Hydrocarbons in Oxygen.*

By John Stanley Lewis.

It is now generally recognised that paraffin hydrocarbons react readily with oxygen at comparatively low temperatures. The temperatures at which rapid oxidation sets in during the slow heating of mixtures of hydrocarbons and oxygen in glass bulbs have been investigated by the author, and some of the conditions noted (J., 1927, 1555; 1929, 759). In the pressure–temperature curves, peculiar increases of pressure occurred at points termed "critical inflexion temperatures" (*C.I.T.*). The slope of the curve above the point of inflexion was influenced by factors such as the rate of heating and the concentration of oxygen and hydrocarbon. This is accounted for by a variation in the velocity of the reactions; increase in concentration caused a more rapid rise in pressure, but on the other hand, a faster rate of heating permitted less time for chemical action to proceed.

The above experiments in slow heating of oxygen–hydrocarbon mixtures occasionally resulted in explosions, and since these occurred at temperatures near the *C.I.T.*, it was surmised that the chemical actions pertaining to the *C.I.T.* were closely connected with explosion or self-ignition temperatures of these mixtures, the main difference being one of velocity. The following work is an investigation of this relationship.

The various methods in use for the measurement of ignition temperatures give discordant results to such an extent that it has become necessary to introduce the qualifying term "relative ignition temperatures" (Mason and Wheeler, J., 1922, **121**, 2079), for comparable values can only be obtained when important governing factors (*e.g.*, material and surface area of the igniting vessel, volume of the chamber, concentration of reacting gases, pressure, etc.) are maintained constant. The current methods can be classified as (*a*) crucible method, (*b*) dynamic tube method, (*c*) bomb method, and (*d*) adiabatic compression of the mixture. The gradual heating of mixtures until explosion occurs does not appear to have been described. It is not suggested that the following method, though simple in design, can supersede any of the foregoing methods, but the results help to illustrate many well-established facts connected with ignition temperatures and the difficulties of obtaining even relative values.

EXPERIMENTAL.

The apparatus consisted simply of a cylindrical bulb (of 125 or 225 c.c. capacity) of good soda glass fitted with a piece of glass tubing 3½″ long, the end of which was corrugated to enable a piece of rubber pressure tubing 4″ long to be firmly attached; the open end of the latter was closed by a stout clip before the mixture in the bulb was heated. The bulb was cleaned with chromic acid and water and dried in a hot air oven by a current of dry air. In an experiment, the cooled bulb was filled with oxygen, and the desired quantity of hydrocarbon was introduced in a small tube drawn off at one end to a sealed capillary, the rubber tubing then being closed with the clip. The capillary was broken when required by shaking the bulb. For experiments of a comparative nature, it is sufficient to measure out the hydrocarbon with a capillary pipette. A bulb of specified dimensions, and filled at atmospheric pressure, being used in a series of experiments, the mass of oxygen remains practically constant.

The conditions requisite for the exploding of the hydrocarbon–oxygen mixtures by progressive heating are (*a*) sufficiently rapid rise in temperature, (*b*) adequate concentration of oxygen, and (*c*) a concentration of hydrocarbon above a certain minimum. At the temperature of explosion the rubber tubing is burst, and occasionally the bulb itself is shattered. The bulbs were therefore enclosed in a copper-gauze cage, and the observer was protected by a plate-glass shield. The explosion temperature is governed by many factors, of which the following have been studied.

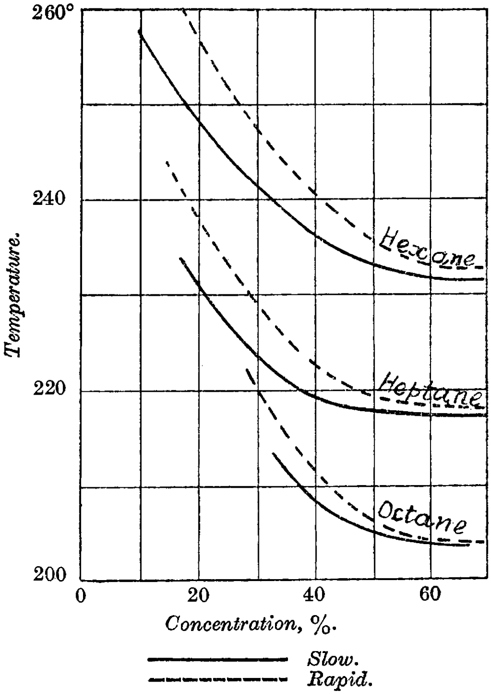
Concentration.—Other conditions remaining constant, an increase in concentration of a paraffin hydrocarbon tends to lower the explosion temperature until a minimum is obtained. For dilute mixtures, results were only reproducible to within 3° or 4° owing to difficulty in adjusting the rate of heating, and as a mean of a large number of experiments the curves in Fig. 1 were drawn; the minimum temperature, however, is correct to within 1°. The curves exhibit certain points of interest.

(*a*) For a particular rate of heating, a minimum concentration is necessary to obtain an explosive action, and more dilute mixtures will not explode. This minimum increases rapidly with rise of molecular weight in the case of paraffins. Thus, with a 225 c.c. bulb and a rate of heating of just under 1° per min., concentrations of hexane below 10% failed to explode, but extensive oxidation had occurred, as revealed by analysis and by the fact that when the exeriment was repeated with a mercury manometer attachment, the pressure–temperature curve showed a well-defined *C.I.T.* at

234—235°. Therefore, it is assumed that, although rapid oxidation had set in at this temperature, the conditions were not such as to give rise to ignition. For octane a concentration of at least 33% was necessary for explosion, whereas all concentrations of *iso*decane (di*iso*amyl) failed to ignite unless a greater rate of heating was employed.

The foregoing affords a rough measure of the ease of oxidation of these hydrocarbons, and, in general, it seems that the minimum percentage for ignition by this method increases with the instability towards oxygen. This applies also to unsaturated hydrocarbons, which will not explode except at high concentrations and rapid rates of heating, the hexylene minimum being much higher than that for amylene.

FIG. 1.



(*b*) The character of the explosion is controlled by the concentration of the original mixture. With rich mixtures a minimum explosion temperature obtains, but in the case of paraffin hydrocarbons the explosion is a mild one with a low note, often an absence of flame, and no carbon deposit—just sufficient pressure has been suddenly generated to burst the rubber tubing. The residual gases in the bulb contain traces of carbon monoxide and dioxide, and the liquid condensed on the walls gives aldehydic reactions. It must be emphasised that the mixture is well outside the usual explosive range of hydrocarbons and in the neighbourhood of equimolecular concentrations. With a reduction in the hydrocarbon content, the violence of the explosion seems to increase until a maximum is reached when the ratio approaches that necessary for complete combustion. In such cases the explosions were sufficiently intense at times to shatter the glass bulb and were always accompanied by flame.

(*c*) The fall of the curves to the minimum is not without significance. The lighter members of the series are more resistant to, or react more slowly with, oxygen; they can be heated well above the minimum ignition temperature, especially in dilute mixtures, and are less liable to pre-ignition in internal-combustion engines.

Rate of Heating.—A more rapid rate of heating tends to raise the ignition temperature. The chemical reactions occurring at the *C.I.T.* are comparatively slow, and in the case of dilute mixtures may be insufficient to give rise to explosion. It will therefore be a simple matter to "superheat," as it were, the mixture to a temperature above the ignition point obtained by a slower rate of heating, thereby accelerating the chemical action and causing an explosion which is far more violent than with the slower speed. An increase in the hydrocarbon ratio has an opposing effect because it increases the velocity of the reaction and tends to lower the explosion point. It will therefore be more difficult to "superheat" rich mixtures above the ignition temperature. These facts are illustrated in Fig. 1, where the variations of ignition temperatures are given for two widely different rates of heating and for various concentrations.

The olefins, however, do not show this great rise of ignition temperature with speed of heating, and, moreover, because they are more readily oxidised, their minimum concentration for ignition is much higher than that of the corresponding paraffin: Thus, for all conditions tried with amylene, the explosion temperatures only varied between 240° and 244°, but even with rich mixtures violent explosions were obtained.

A combination of the two factors already mentioned, *viz.*, a high concentration of hydrocarbon and a slow rate of heating, must tend towards a minimum explosion temperature. These minima can be taken as relative ignition temperatures for many of the hydrocarbons, and Table I contains some results obtained by this method. They are of interest in that they are much lower than the ignition temperatures recorded in the literature, which have been obtained by other methods, and also because they approximate to the *C.I.T.*'s of these hydrocarbons.

TABLE I.

Hydrocarbon.	Minimum ignition temp.	*C.I.T.*
n-Pentane	255—257°	255°
n-Hexane	232—233	230
n-Heptane	218—220	209
n-Octane	203—204	197
*iso*Decane (Di*iso*amyl)	210	—
Amylene	241—242	240
Trimethylethylene	243—244	—
Methylethylethylene	251—252	—
Hexylene	229—230	—

The lowest ignition temperature obtained for *iso*decane (210°) is higher than that of octane (204°). In order to bring about the explosion of *iso*decane, which is very readily oxidised at 200°, it is essential that a high concentration be used and a rapid rate of heating, about 4—5° per min., otherwise the experiment fails. A strict comparison, therefore, can only be made where equimolecular concentrations are subjected to the same rate of heating. Two bulbs containing octane and *iso*decane of about equal concentrations were very rapidly heated in the same bath with sufficient speed to explode them : the former ignited at 217° and the latter at 211°.

Presumably there is no distinction between the *C.I.T.* of a mixture and the explosion temperature, except one of degree. The curves of Brunner and Rideal (J., 1928, 1162) for hexane–oxygen, maintained at constant temperatures below the *C.I.T.*, terminate in a rapid rise in pressure. An examination of the curves (*a*), (*b*), and (*c*) (*ibid.*, p. 1166) reveals the fact that the slope at the *C.I.T.* is more inclined to the vertical, and the angle with the vertical increases with the lowering of temperature. This is as one would expect, since the chemical changes involved decrease in velocity with lowered temperature. It might be reasoned that these changes can be accelerated by concentration, and thus explosive reactions might be obtained below the *C.I.T.* by keeping the gases at a constant temperature. A 50% hexane mixture in a 225 c.c. bulb was maintained at a temperature just below the *C.I.T.* At 228° an explosion resulted, but lower temperatures failed to cause ignition. A weaker mixture, with 35% hexane and immersed in the same bath, also failed to explode. It may happen that the 50% mixture would explode at a still lower temperature if initially compressed, but it is not possible to attempt this in glass bulbs.

Catalytic Actions.—Many investigations have been carried out upon the influence of surface and of positive and negative catalysts on ignition temperatures, but the results are frequently conflicting.

In comparison with metallic surfaces, it is usually stated that glass and silica surfaces have a very low activity on the oxidation of hydrocarbons, so that the result with a plain glass surface will be taken as a zero. This problem of catalytic action is so complex that the following experiments must be regarded as qualitative and introductory. The oxidation of these hydrocarbons proceeds in stages, and it is clear from what follows that the course of the reactions and the nature of the final products are dependent on the surface in contact with the reacting gases.

(a) *Powdered glass.* The ignition point of paraffins is raised in all cases, the amount depending on the rate of heating and the concentration, but variation in the weight of glass between 0·2 and 1·0 g. had little effect. In one set of experiments, the ignition point of octane was raised from 204° to 218° and that of hexane from 232° to 257°, but the differences diminish greatly with rich mixtures and slower temperature rise. On the other hand, the ignition temperature of amylene underwent little change in the presence of powdered glass, but the violence of the explosion was considerably decreased. Powdered pumice behaves similarly.

(b) *Charcoal.* The action of this catalyst is noteworthy in that it affects paraffins and olefins in opposite directions, and the extent varies with the nature of the charcoal. The ignition temperature of paraffins was *raised*, whilst that of amylene was *lowered considerably*; with wood charcoal (0·5 g.) which has been powdered, sieved (60 mesh), and strongly heated in a covered crucible, and with the same rate of heating, 40% mixtures of the various hydrocarbons gave the following results :

Hydrocarbon	C_8H_{18}	C_7H_{16}	C_6H_{14}	C_5H_{10}
Blank expt.	205°	220°	233°	240°
Charcoal present	220	249	254	210

Amylene appears to vary more widely with different charcoals, and explosions at 200°, 210°, and 227° were obtained with three samples. Decolorising charcoal failed to cause an explosion under any conditions of concentration and rate of heating, although the hydrocarbon was considerably oxidised.

(c) *Metals.* Metals may have no effect on the ignition point, or may raise the temperature or even inhibit explosion in some instances, according to the metal employed, extent and condition of the surface, concentration of hydrocarbon, and the speed of heating.

(i) Silver. In one set of experiments the silver was deposited on the inside of the bulb, and in another set a strip of the metal was enclosed. The explosion temperatures were raised considerably in every case; thus, octane gave 204° (blank), 212° (silver coating), and 214° (silver strip).

(ii) Platinum. The results were much as those for silver. Octane gave 205° (blank), 218° (strip), and 212° (coating), whilst hexane gave 232° (blank) and 249° (strip).

(iii) Tin, Zinc, and Aluminium. There was no appreciable rise in explosion temperatures with 4″ × ⅛″ strips of metal with freshly cleaned surfaces. All hydrocarbons in the presence of any one of them detonated within 0—2° of the blank. The metallic surfaces remained bright, and light yellow liquids condensed in the bulb on cooling.

(iv) Lead. The temperature of ignition is considerably raised and explosion may even be inhibited. A 4″ × ⅛″ strip of the metal was heated with 50% octane-oxygen at a rate of about 2° per min. No ignition occurred up to 275°, and examination of the bulb after cooling showed that the surface of the metal had been attacked, yielding a loose greyish powder easily rubbed off; a dark brown viscous gum collected on the bottom of the bulb, but the walls remained clear. When opened under water, the bulb became about three-quarters filled with liquid, and qualitative examination denoted the presence of carbon dioxide and monoxide, a trace of oxygen, and a small remainder of combustible gases that burned with a non-luminous flame.

(v) Copper. This metal also prevented the ignition of octane, but the appearance of the bulb was very different from that in which lead had been heated. A brownish skin was deposited over the whole surface of the glass, and the copper was only tarnished if it had not had a preliminary cleaning, but was blackened by a film of oxide if the surface had been freshly scraped. Opening the bulb under water gave a residue of gas appreciably more than in the experiments with lead, but it was qualitatively similar.

The effect of these two metals diminishes with decrease in molecular weight of the hydrocarbon, and the ignition temperature of pentane was raised only 2° and that of hexane 7° by approximately the same sized strips of metal.

(vi) Iron. A 50% octane mixture was slowly heated with a strip of steel: a violent explosion occurred at 207°, shattering the glass bulb. This was the first instance of such an event with this hydrocarbon, for under all other conditions the bulb remained intact. The surface of the steel remained bright.

The results obtained in the foregoing experiments may be discounted because the metals are coated with oxide films at the temperature of explosions. As will be suggested later, the lag is a far more satisfactory measurement than the ignition temperature, and experiments are now in progress on the effect of metal surfaces and metallic oxides on the time of lag.

(d) *Lead tetraethyl.* The minimum explosion temperature was raised in every case, sometimes as much as 40°, depending on the concentration of lead tetraethyl (up to a maximum effect), the rate of heating, and the surface area of the glass in contact with the gases. The last factor was illustrated by heating 50% hexane–oxygen mixtures in a bulb with various proportions of powdered glass and lead tetraethyl, the rate of heating being the same in each experiment. In presence of 1 g. of powdered glass, the ignition temperature with a 0·9% lead tetraethyl solution in hexane was 260°, and for 0·2 g. of the glass it was 274°. Again, a 0·25% solution of the lead compound raised the ignition temperature of hexane to 269° in the presence of 0·1 g. of powdered glass, but only to 240° with 1·0 g. It is apparent that the ratio of lead tetraethyl to powdered glass is a controlling factor in the rise of ignition temperature, the latter tending to inhibit the action of the lead compound.

The effect of increasing concentration of lead tetraethyl on the explosion temperature of octane is shown in the following results.

$PbEt_4$, %	0	1	2	3	4	5
Explosion temp.	204°	230°	232°	238°	239°	238°

Volume of Bulb.—Two bulbs of 125 c.c. and 225 c.c. capacity were filled with oxygen–hydrocarbon mixtures of as nearly as possible the same composition. They were connected by a piece of pressure tubing and heated in the same bath to about 160°, so that equalisation of pressure (and possibly also of concentration) was effected; they were then separated by clamping the tubing at two points and cutting the rubber between the clamps. Both bulbs exploded within a few seconds of each other on further heating.

Concentration of Oxygen.—It is usually stated that the ignition temperature as determined by the usual method is lower in oxygen than in air, but it must be stressed that other variables are introduced: when determinations are made with air, the oxygen, on account of its lower concentration, may be consumed before explosion is possible; with pure oxygen, a higher concentration of hydrocarbon can be introduced, thereby reducing the explosion temperature to a minimum. When air was substituted for oxygen in the glass bulbs, the hydrocarbons could not be ignited by rapid heating in a bath, although this can be done when the rate of heating is much greater, as in the crucible methods, etc., or when the mixture is suddenly heated in a tube or bomb initially at a high temperature. An atmosphere of 50% oxygen–nitrogen failed to ignite a given weight of hexane heated at a rate of 3° per min., whereas with 75% oxygen content in the bulb originally, explosion took place at 247°. On repeating the latter experiment and comparing it with a bulb containing pure oxygen and the same weight of hexane as a check, the latter exploded at 245°. Many such experiments with paraffins indicated that increase in oxygen content tends to lower the ignition temperature, but the effect is small compared with that of the hydrocarbon. Amylene, however, showed practically no change of ignition temperature when exploded in various concentrations of oxygen. The presence of nitrogen in the lowered concentrations may have some effect, but this has not been investigated. By making a fine slit in the rubber tubing attached to the bulbs, the pressure inside is maintained at atmospheric pressure, but the concentration of both reactants is diminished, and this would be expected to raise the ignition temperature. This was found to be the case, except that a more rapid heating is necessary to cause explosion; thus, hexane exploded at 256°. These results were more comparable with those obtained by the crucible method, and some experiments of the latter kind were carried out in test tubes, the effect of the same factors being investigated.

Test-tube Experiments.—Air. The tubes were almost wholly immersed in an oil-bath at the required temperature, and drops of the liquid were allowed to fall into them from a capillary tube, the quantity being varied until lowest ignition was obtained. Experiments with *closed* and *open* mouths proved that the former gave much lower ignition temperatures with air and oxygen. Thus, in a 7″ × 1″ test-tube the minimum ignition temperature in air for octane was 225—226°, and 214° when a tightly fitting lid was applied—the mouth of the test-tube was ground down to a level surface and the lid smeared with plasticine to make it air-tight. Various numbers of drops of octane were introduced at decreasing temperatures until no signs of ignition or rapid oxidation occurred. Between each trial the residual gases in the tube were blown out and any signs of carbon deposit removed. Ether was found to ignite at 183—184° by such a method in a 7″ × 1″ tube. For the final tests, it is essential that freshly cleaned tubes be used each time in order to obtain the lowest ignition point.

These experiments are noteworthy since they emphasise the facts that there is no line of demarcation between the rapid oxidation temperature and the ignition point, and that the time of lag can be much longer than is generally supposed. At temperatures well above the ignition point, the lag is comparatively short, and the flame and characteristic sound of explosion well defined, but as the temperature is lowered these become less definite and the time for their appearance much longer. By using the covered-tube method, the author obtained lags of over 500 secs. on many occasions with rich mixtures of hydrocarbons dropped into oxygen. Under such conditions no explosion sound can be heard, but a slight puff which pushes up the lid slowly, and furthermore, there is no apparent flame.

The diameter of the test tube is also an important factor, although beyond 7″ the length had no appreciable effect. With the 7″ tubes, the ignition point was at first lowered with increased diameter but was subsequently raised with still wider tubes, although the concentration of hydrocarbon was increased proportionately, thus :

	Ignition temp. in air for	
Diameter.	octane.	hexane.
0·75	221°	271°
1·00	214	265
1·25	216	268
1·50	219	269

Oxygen. Ignition temperatures in oxygen are lower than in air; thus, for a 7″ × 1″ tube, the following results were obtained.

Hydrocarbon	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_5H_{10}
Temp. in air	305°	265°	247°	214°	—
,, oxygen	295°	248°	235°	207°	270°

Powdered glass and pumice. The ignition temperature is raised, depending on the weight of powder, up to a maximum on the molecular weight of the hydrocarbon (or, more correctly, its ease of oxidation). Thus, the increase for the same weight of pumice is more for octane than for hexane.

Charcoal. The temperature of paraffin hydrocarbon ignition in oxygen is raised; thus in 7″ × 1″ tubes, 0·2 g. of charcoal required a temperature of 221° to ignite octane and 254° for hexane. Amylene exploded in oxygen alone at 270°, but at 268° in the presence of charcoal. The concentration of amylene required to bring about explosion is always much higher than that of paraffins.

Metals. These may be classified as (*a*) those having little effect, such as aluminium, tin, and zinc (see above), and (*b*) those promoting oxidation and raising the ignition temperature, such as platinum, copper, and lead, the effect being greater the lower the molecular weight. Interesting results were obtained with a copper test-tube 6″ × 1″, the inner surface of which had been cleaned and polished. The ignition temperature of octane in air was 223° at first, but after repeated experiments the readings were much higher, and even in oxygen the hydrocarbon would not ignite at 225° after such treatment. It is evident that deposits interfere with successive results, and the surface must be renewed for each experiment. When this was done, the original value of 223° was obtained.

Lead tetraethyl. As in the previous experiments, the temperature of ignition was raised in all cases, *e.g.*, hexane in air to 283° by a

1% concentration of the lead compound, the lag being nearly 300 seconds. The addition of powdered glass or pumice reduces the ignition temperatures and the lag. The latter at 278° was 250 secs. for 0·2 g. of powdered pumice, but ignitions were obtained as low as 273° with 1·0 g. of pumice.

Discussion.

Mason and Wheeler (*loc. cit.*) have pointed out that when such mixtures as have been used in the foregoing experiments are gradually heated, the rate of combination of oxygen and hydrocarbon increases; and so the heat evolved by the reaction raises the temperature of the products and unburnt gases above that of the external source of heat. There will be a tendency for the rate of reaction to increase until the whole of the hydrocarbon or oxygen is consumed. When, however, the initial temperature imparted to the walls of the vessel is sufficiently high, the rate of reaction will become so rapid as to produce flame. This statement is only partially true, and the above observations apply to experiments in which oxygen–methane mixtures were allowed to enter an evacuated silica bulb maintained at a comparatively high temperature, so that the mixture is heated much more rapidly than in the present experiments. The heat of the reaction at this high temperature cannot be dissipated as quickly and will undoubtedly be utilised in raising the temperature of the contained gases and hence the velocity of their reaction, which will become explosive. It is incorrect, however, to state that oxygen–hydrocarbon mixtures react with gradually increasing velocity with rise of temperature as suggested above, because the author (*loc. cit.*) has shown that there is a definite transition from slow chemical action to rapid action at a temperature which has been termed the *C.I.T.*, and Brunner and Rideal (*loc. cit.*) have proved that for hexane–oxygen mixtures this rapid change may take place at still lower temperatures when the mixtures are maintained at constant temperatures for lengthy intervals. The transition from very slow oxidation to explosion is still far more abrupt when anti-oxidants are added, such as lead tetraethyl, which reduces the reaction considerably almost up to the temperature of explosion. Moreover, neither the "lag" interval nor the catalytic effects of promoters and inhibitors of oxidation receive a satisfactory explanation from the above statement.

In order to account for such facts as the last, the theory of chain mechanism has recently been applied to the combustion of hydrocarbons, notably by Egerton and Gates (*J. Inst. Pet. Tech.*, 1927, 281; *Nature*, 1928, **121**, 10) and also by Brunner and Rideal for hexane (*loc. cit.*). The latter workers have measured the amounts of peroxides or " moloxides " of hexane during the period of autoxidation, but the author believes that these peroxides are produced from the unsaturated hydrocarbon initially formed by primary dehydrogenation (see Part I; J., 1929, 759). Further, the fall in pressure noted by these authors for hexane--oxygen at 210° is not definitely proved to be a measure of the moloxide formation. Similar experiments have been repeated with silica and glass bulbs and the pressure drop in the former is appreciably less, indicating greater surface action with glass. The amount of gummy residue was larger in the glass bulb, and this would suggest that the fall in pressure is chiefly due to the formation of condensation products. In the case of unsaturated hydrocarbons, this fall of pressure is much more pronounced (see Part I) and leads to the conclusion that the chemical change involved is the same, although the velocity differs, being much greater for amylene. The primary dehydrogenation would therefore be a comparatively slow reaction, especially at first (see Part I), and probably takes place in the gaseous phase. This would account, in part at least, for the fact that metallic lead has no inhibiting action whilst lead tetraethyl vapour is particularly effective at this stage of the oxidation, if one could assume (in spite of some adverse opinions) that the vapour of lead resulting from the decomposition of the tetraethyl is the active component. It is also significant that this anti-oxygen does not inhibit the oxidation of amylene to the same extent as that of pentane.

The successive stages in the combustion of paraffin hydrocarbons suggested by the author are : (*a*) primary dehydrogenation resulting in unsaturated hydrocarbons, (*b*) combination of the latter with oxygen to produce unstable peroxides, (*c*) decomposition of the peroxides *per se* to aldehydes, etc., which are further oxidised to water and oxides of carbon if the mixtures are rich in oxygen. The velocities of these step reactions probably vary widely in themselves and still more so in the presence of catalysts. According to the chain-reaction mechanism, then, when hydrocarbon–oxygen mixtures are slowly heated, as in the experiments of the author and of Brunner and Rideal, or during the " lag " interval present in the determination of auto-ignition temperatures, there will be an increase every moment of the active centres present due to one cause or another, and after a certain lapse of time, which may extend to several minutes as shown in the experimental part (autoxidation), they may be present in such concentration as to give rise to rapid pressure increase without flame or even to explosion. The reaction is exothermic, and when approximately equimolecular concentrations are used, the products are chiefly aldehydic, acid, or gummy, with very small proportions of the oxides of carbon and water. If there is present a large excess of oxygen, the oxidation becomes far more violent and complete, owing to the liberation of heat in this initial reaction, which raises the temperature of the whole system and brings about the further oxidation of the peroxide decomposition products.

An increase in concentration of hydrocarbon tends to reduce the auto-ignition temperature (see Mason and Wheeler, J., 1924, **125**, 1869), whereas the oxygen concentration produces a much smaller effect. These authors attribute this phenomenon to the fact that the component with the greater " stopping power " for radiant energy such as will " activate " it, increases the rate of reaction with the concentration. Or, according to the chain mechanism, the increase of hydrocarbon molecules is said to augment the number of chains formed in unit time and hence the number of active centres. The oxygen concentration lowers the ignition to a much smaller extent, as pointed out above. Moore (*J. Inst. Pet. Tech.*, 1919, 186) added 70% of carbon dioxide to the oxygen, and, using a platinum crucible method, found an inappreciable difference in the ignition temperature of kerosene. White and Price (J., 1919, **115**, 1462) and Mason and Wheeler (*loc. cit.*), using two different methods, obtained appreciable changes with variations in the air/fuel ratio; they did not actually study the effect of oxygen concentration, since the mass of fuel was not maintained constant. The auto-ignition temperature, then, is a function of the concentration of hydrocarbon and, to a much smaller extent, of oxygen. If either or both of these are consumed during the pre-flame period, no ignition obtains. Insufficient active centres have been produced, or, in other words, the accumulation of peroxides has been too slow and one or the other of the reactants has disappeared before ignition occurs. Hence it will be necessary to raise the temperature of the mixture of similar composition in order to accelerate the formation of active centres in unit time, *i.e.*, the autoxidation, and thus produce an explosion. The lag has been decreased. It should follow from the above view that the ignition temperature of a given mixture will be lowered by an increase in pressure, but very little work has been done on this subject. There is a possibility that the effect of increased concentration by pressure would be nullified at a lower temperature by the reduction in the rate of formation of reactive centres, so much so that these would be deactivated before explosion could occur; this would to a certain extent reduce the effect of increased pressure.

The effect on the ignition temperature of various materials has received much consideration but results are at variance (Moore; White and Price, *locc. cit.*; Egerton and Gates, *J. Inst. Pet. Tech.*, 1927, 244); for paraffin hydrocarbons, however, the author proves that some metals, such as aluminium, tin, nickel, and zinc, have little if any effect upon the explosion temperature, whereas others, such as silver, iron, platinum, copper, and lead, raise the temperature of ignition and may even prevent the explosion. It is suggested that this is brought about by the removal of the peroxides on the surface of these metals, yielding aldehydes or their polymerised products (gums), the exact nature of the decomposition being determined by the temperature and the nature of the metal employed. An increase in the number of chains broken in unit time may be said to have been taking place on the metallic surfaces. The same result is brought about by an increase in the surface of the glass in contact with the gas, which will account for the rise in explosion temperature occasioned by the presence of powdered glass and pumice, or the etching of the internal surface of the vessel. The action of carbon on the paraffins and olefins is noteworthy. Towards the former it acts similarly to powdered glass and pumice in raising the ignition point. The powdered charcoal is a strong absorbent; it is also reputed to be a destroyer of peroxides, and since these are readily formed by olefins, the rate of oxidation and the heat evolution may be so rapid as to give rise to local ignition, which will account for the low ignition point of amylene at a charcoal surface.

In the glass-bulb experiments, the difference in the ignition temperatures with change of volume from 125 c.c. of 225 c.c. was inappreciable probably owing to the high concentrations of oxygen and hydrocarbon. In closed glass tubes of various diameters, White and Price (*loc. cit.*) found that the temperature decreased at first and then increased with increasing diameter of the tube. The test-tube method indicated a similar result, but it is apparent that when narrow test-tubes are used the initial concentration of the reactants will be small and one or the other will be consumed before the desired concentration of active centres is attained.

The results with lead tetraethyl confirm those of Egerton and Gates (*J. Inst. Pet. Tech.*, 1927, 244) and of Weerman (*ibid.*, p. 300), but if, as the former point out, anti-knocks do influence the ignition temperatures, it will not follow that the converse is true, *viz.*, that substances which raise the ignition temperatures of a fuel are anti-knocks (compare the action of carbon). The action of the above inhibitor in the presence of powdered glass or pumice is noteworthy. It has been shown that an increase in the surface thus produced tends to reduce the inhibitory action of the lead tetraethyl, probably owing to an increase in the rate of oxidation. It must be emphasised that the rises of ignition temperatures brought about by this reagent are entirely different from the foregoing. Lead tetraethyl is a negative catalyst, or anti-oxygen, and delays or inhibits even the initial stage of oxidation, so that very little change occurs in the hydrocarbon at temperatures somewhat higher than the normal ignition point. On the other hand, lead and copper, powdered glass and pumice are promoters of oxidation by surface action and bring about the rise of temperature by a removal of a fraction of the products in one stage of the oxidation which give rise to the explosion.

The spontaneous ignition temperatures are not related to the detonation characteristics of a fuel; thus, the unsaturated hydrocarbons with less knocking tendencies have lower explosion temperatures than the corresponding paraffins. Brown and Watkins (*J. Ind. Eng. Chem.*, 1927, **19**, 368) found that the ratio of the maximum rate of rise of pressure to the ignition temperature (absolute) gives a number which rises directly as the knocking quality of the fuel or inversely as Ricardo's "highest useful compression ratio" (*H.U.C.R.*). The estimated *H.U.C.R.*'s of paraffins and aromatics agree fairly well with those practically determined, but no figures are given for unsaturated hydrocarbons. Since these have correspondingly lower ignition temperatures, it should follow that their maximum rate of rise of pressure is less than that of the corresponding paraffin, and the testing of this point would help to elucidate the problem. In order that fairly accurate results may be obtained for the above ratio, it is essential that the data for autoignition be fairly trustworthy. Oftentimes discrepancies are found in the published results, *e.g.*, octane having a higher ignition temperature than heptane, and heptane than hexane. A similar result is shown for decane and octane above, but this is readily explained by the greater oxidisability of decane which is consumed at low temperatures on the surface of the glass, or, in terms of chain mechanism, the deactivation exceeds the rate of chain formation at the lower temperatures, so that it is difficult to make it explode by slow heating. A strict comparison with octane can only be made with equimolecular concentrations of hydrocarbons, equal area and nature of surface, and equal rate of heating. Under such conditions, octane has been shown to ignite before decane, although the rate of heating required for the latter to explode is so rapid that the ignition temperature of octane is somewhat raised above its minimum. The anomalous results obtained by the crucible methods can be explained in a similar manner : the droplets may not have yielded equimolecular concentrations, the rates of heating at the two temperatures are not the same, and at the temperature at which one might expect ignition, the hydrocarbon has been completely removed by flameless or surface combustion, especially when platinum has been used and the drops have been small. Hence, one unhesitatingly concludes that the method of determining the relative ignitabilities by the measurement of the duration of the pre-flame period or " lag " at a temperature higher than the ignition temperature is to be preferred to the " crucible " experiments. Some of the paraffins have been compared by Mason and Wheeler (J., 1924, **125**, 1873) by this method.

The view is prevalent that fuel droplets ignite more easily than the vapour, and this is attributed to the accumulation of peroxides in the liquid drops (Callendar, *Engineering*, 1927, 147). Since extremely low ignition temperatures can be obtained when the concentration of the hydrocarbon and oxygen is high, it is reasonable to suppose that the ignition of the droplets in the above experiments has been favoured by the richness of the vapour–oxygen atmosphere surrounding each liquid particle, thereby bringing about the conditions for the minimum ignition temperature. No significance can be attached to the fact that, when a fuel is sprayed or vaporised through a heated tube, the spray gives rise to a profusion of peroxides whilst the vaporised mixture shows little effect. If peroxides are produced in one stage of the oxidation, this will probably be at the surface of the droplets where they would be absorbed by the comparatively cool liquid and thus preserved. On the other hand, when vapour only is present, the peroxides would eventually come in contact with the heated walls of the tube, with resultant decomposition.

Summary.

A simple preliminary apparatus has been used to find the conditions and temperature of ignition of mixtures of some hydrocarbons and oxygen, and a mechanism of the reactions has been considered.

Spontaneous ignition temperatures, as determined by the usual methods, are raised by materials, such as lead tetraethyl, which inhibit oxidation or reduce autoxidation, in that they diminish the number of fresh chains formed in unit time, whereas promoters of oxidation by surface action raise the temperature of ignition by removing one of the intermediate products, presumably peroxides, or alternatively, according to the chain mechanism theory, they increase the rate of deactivation.

The disturbing factors in the determination of relative ignition temperatures are so numerous that the measurement of the " lag " in the case of equimolecular concentrations at some point above the ignition temperature is to be preferred as a measure of the ignitabilities of hydrocarbons.

The explosion of hydrocarbons takes place in two stages : (*a*) the

explosion of the products of autoxidation (peroxides or chain reactions, in which approximately equal number of molecules of oxygen and hydrocarbon participate), and (*b*) the combustion of the products of stage (*a*) in excess of oxygen to oxides of carbon and water.

ROYAL NAVAL COLLEGE,
GREENWICH, S.E.10.

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