CCVI.—*Low Temperature Oxidation of Hydrocarbons.*

By JOHN STANLEY LEWIS.

IN his researches on the combustion of methane and ethane, Bone proved conclusively that reaction with oxygen takes place at temperatures well below the ignition point, the products being aldehydes.

water, etc. As a result of this work he put forward his hydroxyl theory (J., 1902, **81**, 535; 1903, **83**, 1074; 1904, **85**, 693, 1637; *Proc. Chem. Soc.*, 1905, **21**, 220). More recent work has shown that paraffin oils and waxes undergo oxidation at low temperatures, and the latter have been converted into fatty acids, but attention has been given also to the unsaturated hydrocarbons, especially diolefins, which are prevalent in " cracked " spirit. A review of the work on " Gasolines " is given by Brooks (*Ind. Eng. Chem.*, 1926, **18**, 1198). An advance has been made by Callendar (*Engineering*, February, 1927), who has proposed the theory that the initial step in the oxidation of paraffins at low temperatures is the formation of peroxides which decompose eventually into aldehydes, acids, water, etc.

The present paper contains an account of (*a*) a simple arrangement for determining the temperatures of initial oxidation of paraffin hydrocarbons at constant volume; (*b*) the influence of certain factors upon these temperatures; (*c*) a proposed mechanism of the reaction, which may be called the " primary dehydrogenation theory " ; and (*d*) an attempt to apply this theory to account for the instability of paraffin hydrocarbons as measured by their ignition and detonation characteristics.

EXPERIMENTAL.

Molecular Weights at High Temperatures.—The determination of molecular weights by the Victor Meyer method at temperatures above 200° gives anomalous results for paraffins, the molecular weights decreasing as the temperature increases (Ormandy and Craven, *J. Inst. Petroleum Tech.*, Nov., 1925), as shown in Table I.

TABLE I.

Molecular-weight determinations (Ormandy and Craven).

Temp.	Heptane.	Shell.	Pratt's.	Benzene.
200°	102	100	97	77
220	73	96	96	76
250	79	98	95	78
265	74	80	78	75
275	70			
275 (plus piece of porous pot)	78			

The suggested explanation of this decrease is that chemical action of some kind has taken place causing an increase in the number of molecules, and the above workers attributed this partly to the cracking of the paraffins, and to partial combustion whilst the spirit remained in the liquid phase, vapours being affirmed to be more stable. Experiments conducted with coal-gas gave more normal results. The foregoing results have been disputed by some workers, but they have been confirmed in this laboratory, and some of the results obtained for hydrocarbons other than paraffins are shown in Table II.

TABLE II.

Molecular-weight determinations of typical hydrocarbons.

Benzene.		Toluene.		*cyclo*Hexane.		Amylene.	
Temp.	*M.*	Temp.	*M.*	Temp.	*M.*	Temp.	*M.*
198°	78·6	187°	92	230°	85	200°	72
240	78·4	360	92	260	83	254	73
285	79·8	400	93	342	68	297	60
350	78·4	310 (in oxygen)	93	362	61	295 (in nitrogen)	72
360 (in oxygen)	78·8	385 (in oxygen)	93	400	73	303 (in nitrogen)	70
				400 (in oxygen)	Exploded.	310	65
				400 (in nitrogen)	85	355 (in oxygen)	Exploded.

The aromatic substances are apparently stable up to 400° in these experiments, whereas the olefin and the naphthene are affected by oxygen, but not by nitrogen, and their molecular weights are normal. This seems to discount the view that cracking takes place to any appreciable extent, and experiments are in progress on the lines described later to ascertain the exact temperatures at which the various hydrocarbons crack, and thus to obtain comparative values for their stability in the absence of oxygen. Increase in the expected volume of gas, *i.e.*, decrease in the measured molecular weight, is to be attributed to oxidation, but this oxidation can and does take place in the vapour phase, as will be shown later. It was observed also that the tubes used for weighing the liquid always contained films of gums or tarry deposits at the end of the experiments; these were light brown for low temperatures, and deepened to black tars as the temperature of experiment was increased. These gums are probably formed during cooling and are the condensation products of aldehydes.

The results of the earlier molecular-weight determinations were erratic and variable owing to the fact that the weights of liquid in each experiment differed, thus altering the ratios of hydrocarbon to oxygen and to the surface area of the Victor Meyer bulb. By using the same weighing tube throughout, with approximately equimolecular proportions of liquid for each temperature, and a large bulb, more concordant results were obtained, the observed molecular weights of hexane and octane decreasing gradually with rise of temperature above a certain limit. A fairly smooth curve was thus recorded for temperature–molecular weight (Fig. 1). The figures are in Table III.

TABLE III.

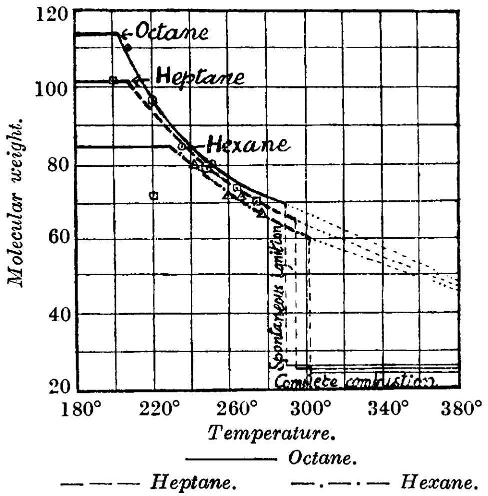
Molecular weights of paraffins, obtained by using constant proportions and conditions.

Hexane.		Heptane.*		Octane.	
Temp.	*M.*	Temp.	*M.*	Temp.	*M.*
200°	87	200°	102	180°	113
242	80	220	73	204	110
260	72	250	79	220	96
266	72	265	74	238	84
278	67	275	70	256	80

* Ormandy and Craven (*loc. cit.*).

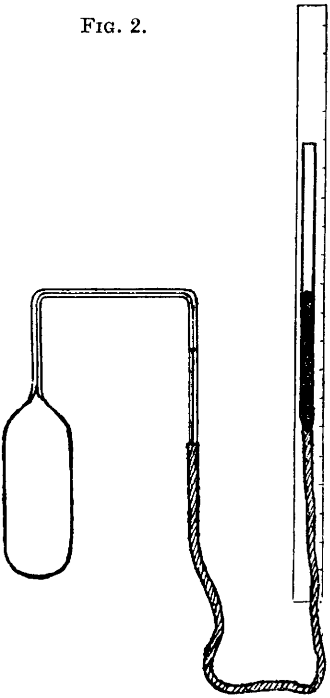
These curves meet the horizontal line of constant molecular weight at a point corresponding approximately to the temperature of initial oxidation. At the other extreme the curves presumably intersect the horizontal lines corresponding to the molecular weights that would be attained if oxidation to water and carbon dioxide was complete; but before this temperature could be reached spontaneous ignition would take place, as indicated diagrammatically by the vertical lines. The above method is obviously unsatisfactory for determining the exact temperature at which oxidation is initiated, and the following simple method was used.

FIG. 1.



Constant-volume Method.—A known quantity of the liquid was enclosed in a large cylindrical bulb to which was attached a stout capillary tube connecting with a mercury manometer, as in the usual form of an air thermometer (Fig. 2). During the slow heating of the bulb, the manometer was raised constantly so that the mercury in the capillary tube was kept at a constant mark, the height of the mercury in the manometer plus the barometric pressure being the pressure of the mixture inside the bulb. Readings were taken at small intervals of temperature, and a pressure–temperature diagram was drawn. If no chemical action takes place the curve should follow approximately that of the gas laws, but in the case of the paraffins there occurs a sudden rise or inflexion indicating chemical action. The temperature at which this rise occurs will be known as the " critical inflexion temperature " or the *C.I.T.* Typical curves are given in Fig. 3. Most of the hydrocarbons used in these experiments were either Kahlbaum preparations or of a purity complying with the recognised physical data. The following results were obtained: Pentane, 253°; hexane, 232°; octane, 198°. (It is possible to read the *C.I.T.*'s to within 1° or 2°.)

FIG. 2.



The initial part of the curve follows the air-thermometer curve approximately until the *C.I.T.* is reached, and once this is passed there is no rapid rise of pressure corresponding to a reaction with increased number of molecules. In fact, for some distance the curve does not differ much from the air curve, having a tendency to fall below rather than to rise above it, as though molecules were combining and becoming fewer in number. At much higher temperatures the curves revealed a progressive, but slow, decomposition. The form of the curve is unexpected, because the sudden rise at the *C.I.T.* denotes a reaction which is completed at this temperature, accompanied by an increase in the number of molecules. Hydroxyl or peroxide formation would cause a decrease in the number of molecules, and hence a depression in the curve, unless these oxygen derivatives were produced and decomposed at the same

FIG. 3.

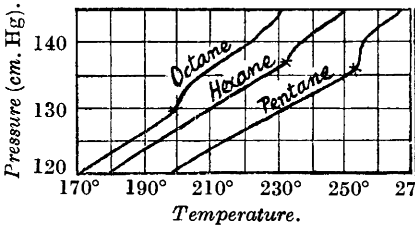
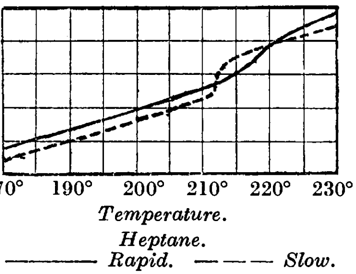


FIG. 4.



temperature. That the whole of this reaction takes place at the *C.I.T.* was proved by maintaining the temperature constant for some time, whereupon the pressure increased to a maximum and remained stationary.

It appears that for paraffin hydrocarbon–air mixtures there is a critical temperature at which rapid chemical action takes place with an increase in the number of molecules.

The critical temperature is dependent upon molecular weight, as seen in the results for pentane, hexane, and octane; but other factors influence it and the following experiments were instituted with a view to determine them.

Rate of Heating.—Two experiments were carried out with heptane, the rise of temperature in one case being extremely slow, and in the other about 1° per minute, the same bulb and equal quantities of liquid being used. The initial parts of the curves are parallel up to the *C.I.T.*, indicating that if chemical action has taken place the extent is the same for the two rates of heating. At the *C.I.T.* the rise for slow heating is more abrupt and is completed within 1° or 2°. That the reaction occurs with measurable velocity is shown by the curve for rapid heating (Fig. 4). In the case of pentane, which has a higher *C.I.T.*, the velocity of the reaction is greater, and with a rate of heating comparable with that denoted as " rapid " above, reaction is completed in a small range of temperature. It may be justifiably concluded that when one of these paraffin hydrocarbon–air mixtures is suddenly raised to a temperature well above the *C.I.T.* but below that of spontaneous ignition, as, *e.g.*, during sudden compression, the chemical change involved at the *C.I.T.* will take place almost instantaneously, giving rise to a pressure higher than the calculated, and also causing evolution of heat.

Concentration of the Vapour.—At first it was thought that concentration played no part, because the differences obtained were very small. To test this point, one bulb was used for a set of experiments in which gradually increasing weights of octane, and also hexane, were employed. The results for octane, depicted in Fig. 5, show that concentration affects the *C.I.T.* to a small but appreciable extent.

It is possible that chemical reaction begins below the *C.I.T.*, but if so, it must be very slight, because on heating some of the mixtures to temperatures below the *C.I.T.*, cooling, and reheating, the curves obtained were almost identical, but on occasions the contents of the bulb reduced a very weak solution of potassium permanganate. No " gumming " or coloration of the finally cooled liquid occurred, however, in any instance.

Atmosphere of Oxygen.—The curves for hydrocarbon–oxygen mixtures were of the same nature as for air. The bulbs were filled with oxygen, a measured quantity of hydrocarbon was added, and pressure–temperature curves were determined as before. These curves varied only in the fact that the *C.I.T.* was more abrupt and completed within a smaller range of temperature (1—2°), showing that, whatever chemical change is taking place at the *C.I.T.*, the velocity is much greater in oxygen. The actual temperature, however, differed very little from that in a similar determination with air, and no more than would be expected from the change in the concentration ratio of vapour–oxygen to vapour–air.

A remarkable feature is that once the *C.I.T.* is passed, the contents of the bulb are apparently stable at least up to 450°, and have been heated to this point without explosion or spontaneous ignition occurring. Callendar, in his tube experiments, heated a paraffin–air mixture to 666° before ignition was reached, but slight explosions occurred at 516° with flashes of flame when the same mixture carried liquid drops of the hydrocarbon. It appears, therefore, that the liquid phase is more unstable than the vapour state, and the *C.I.T.* has some bearing upon this phenomenon. Spontaneous-ignition temperatures for liquid particles must give results which are far below those for complete vapour–air or oxygen mixtures.

Atmosphere of Nitrogen.—Hexane was heated in the apparatus, which had been filled with nitrogen, and up to 365° the pressure–temperature curve was normal and showed no inflexion. No gum was formed and the liquid remained colourless on cooling. On reheating, the pressure–temperature curve was practically identical with the first, thus confirming the work on molecular-weight determinations in nitrogen and the conclusion that no decomposition or " cracking " takes place. The sudden rise in pressure at the *C.I.T.* can only be attributed to oxidation of the paraffin–hydrocarbon molecules, accompanied by an increase in the final number of molecules.

Comparison of Isomerides.—Spontaneous-ignition tests are untrustworthy for making a comparison of the stability of the hydrocarbons in the presence of oxygen, and the recorded results are very variable. The method adopted in these experiments is suitable for comparing two isomerides if the *C.I.T.* is taken as the initial oxidation temperature. Thus in the case of *n*- and *iso*-pentane, when equal weights were heated separately in the same bulb, the *C.I.T.*'s were : Pentane, 253° ; *iso*pentane, 260°.

In this experiment the *n*-pentane is less stable than its isomeride, and if there is a relationship between this temperature and spontaneous ignition and detonation, then pentane should detonate more readily in the engine. It has been shown that an *iso*octane possesses much feebler detonating properties than *n*-octane (Graham Edgar, *Ind. Eng. Chem.*, 1927, **19**, 145).

Surface Area.—The bulbs used were of good soda glass; the effect of surface area is shown by the *C.I.T.* in the following results :

Hydrocarbon.	Large bulb.	Small bulb.
*iso*Pentane	259—260°	263—264°
Heptane	210—212	214—215

Catalysts.—Two typical catalysts were used : (*a*) platinum, an oxidising catalyst, and (*b*) lead tetraethyl, a poison or negative catalyst.

FIG. 5.

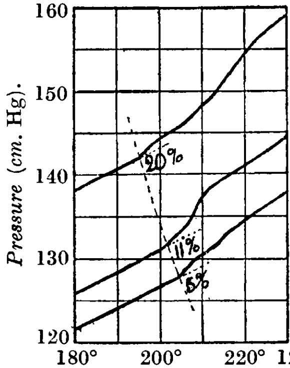
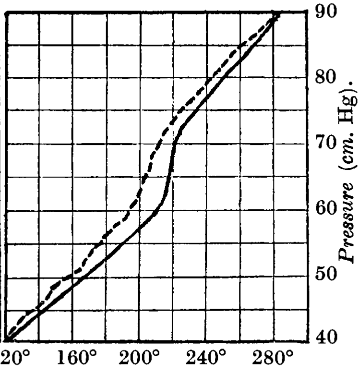


FIG. 6.



Temperature.

———— *Heptane alone.*

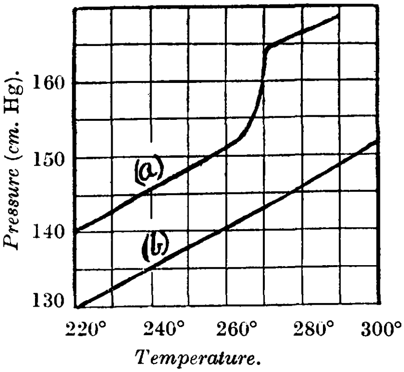
— — — *Heptane with platinum as catalyst.*

(*a*) *Platinum.* This was used both in the form of a coating on the bulb and as platinised asbestos. The effects were very marked : chemical reaction proceeded slowly even at low temperatures, and the pressure–temperature curves showed much irregularity. A typical example of the curves is found in Fig. 6, for heptane, both with and without the catalyst. When the catalyst is present there is a steady rise in pressure above the normal curve, commencing at about 130—140°. Chemical action must be proceeding at or below this temperature. Heating was continued up to 275°; here an unexpected change took place, which must be regarded as a kind of rapid combustion, not an explosion or detonation. The mercury was pushed down the capillary tube with considerable speed, and when it was brought back to zero by raising the manometer, a big increase of pressure was registered. Thereafter, the curve proceeded normally. At the end of the experiment, the bulb was coated with a carbon deposit, and the remaining gases contained carbon monoxide and dioxide. There was none of the usual peculiar smell after heating in the bulbs nor any gummy residue.

(*b*) *Lead tetraethyl.* The remarkable inhibiting properties of this substance were very evident: in every case examined, it either completely obliterated the inflexion in the pressure–temperature curve, or, if a rise did occur when smaller quantities were used, this took place at higher temperatures but was exceedingly small, denoting only slight chemical change with increase in number of molecules. The effect of lead tetraethyl, therefore, is to prevent or reduce that particular chemical change which occurs at the *C.I.T.* A typical example illustrating this fact is given in Fig. 7 for *iso*-pentane, which normally gives a well-defined and easily observed rise of pressure at the *C.I.T.*, but in the presence of 1% of lead tetraethyl there is no sign of a break in the curve up to the highest temperature studied, *viz.*, 298°. On cooling the tube, no gum formation was obtained and the characteristic odour of the oxidation products was absent. In some cases, the bulb was cooled and reheated, and the second curve was then generally in close agreement with the first.

The inhibiting action of lead tetraethyl in oxidation appears to be more general, as the following examples show. The gumming of cracked spirit is attributed chiefly to the formation of peroxides by the "dienes" present. More than a year ago, two samples of cracked spirit were enclosed in glass cylinders, only one of them containing 1% of lead tetraethyl, and at the present time this remains clear and colourless, whilst a thick gum has collected at the bottom of the untreated sample, which is now yellow. These results seem to support Callendar's statement that the action of the lead tetraethyl is to prevent the formation of peroxides. The conditions are, however, entirely different in the two experiments: in the one just described, the temperature is that of the room, and therefore the lead tetraethyl remains as such; at high temperatures it is decomposed, and any negative action must be exerted by the lead itself.

FIG. 7.



(a) *iso**Pentane without lead tetraethyl.*
(b) " *with* " "

A second experiment was carried out with equal volumes of a light lubricating oil contained in four separate flasks. No. 1 flask was heated to 250° with constant stirring, and then cooled. It had darkened rapidly and become almost opaque. No. 2 contained lead tetraethyl and during the same treatment underwent little change except in colour (from light yellow to a light reddish tint), but was otherwise quite transparent. The oils in Nos. 3 and 4 flasks, of which only the former contained lead tetraethyl, were exposed to sunlight for some weeks. The latter darkened gradually, and the final appearances of these samples were identical with those of Nos. 1 and 2, which had been heated. In all cases a solid was deposited after several months' standing.

Further evidence of the negative catalytic action of lead tetraethyl is given by dynamic oxidation tests. Air (free from carbon dioxide) was passed through the oil heated to a known constant temperature, then through a series of U-tubes, two empty for collecting light oily products and part of the water, two filled with calcium chloride, and one with soda lime for carbon dioxide estimation. Experiments were carried out (i) heating the oil alone without air bubbling through, (ii) passing air through the heated pure oil, (iii) passing air through the heated oil containing 1% of lead tetraethyl. The weights of carbon dioxide and water produced were determined, and the oil after treatment was examined quantitatively for hard asphalt, coking test (R.A.F.), and acidity. The first experiment was carried out at 200° for 12 hours, and the rate of air flow was 15 litres per hour. The untreated oil darkened very rapidly, becoming almost black, whereas the sample containing lead tetraethyl remained pale yellow for more than 3 hours, after which it darkened slowly, showing that the catalyst was gradually losing its effectiveness. The coking tests, etc., indicated that the treatment was too severe for this oil; the experiments were therefore repeated at 180° with an air-flow of 10 litres per hour, and were stopped at intervals of 2 hours for analysis of the oil and for the weighing of the water and carbon dioxide. These results are in Table IV, and two points are brought out clearly, *viz.*, the inhibiting action of lead tetraethyl (which, however, decreases slowly), and, secondly, the fact that water is produced during oxidation, but is partially suppressed by the lead tetraethyl. This second point seems to favour the theory of primary dehydrogenation, to be discussed later.

Moisture.—When hydrocarbon–air mixtures were heated with appreciable quantities of water, the pressure–temperature curves were peculiar in that they were exceedingly irregular, even for temperatures just above the boiling point of water, and appreciably higher than the normal curve. Apparently water exerted some chemical or catalytic action, and it was decided to try the effect of eliminating moisture. Accordingly, the bulb was dried as far as possible by heating it in a current of dry air; it was then filled with

TABLE IV.

Changes in a light spindle oil due to oxidation.

Conditions of test.	Viscosity * (secs.).	Coking test (mg. per 100 g. of oil).	Hard asphalt, %.	Acidity (mg. per 100 g. of oil).	H_2O evolved, %.	CO_2 %.
(*a*) Original oil	214	0·34	Nil.	9	—	—
(*b*) Heated at 200° for 12 hrs.	261	0·60	Negl.	14	—	—
(*c*) Heated at 200° for 12 hrs., and air passed through at 15 litres per hr. ...	520	2·63	3·96	97	6·37	0·556
(*d*) As in (*c*) but 1% of $PbEt_4$ added	370	2·02	0·44	47	3·41	0·397
(*e*) Heated to 180°; air passed through at 10 litres per hr. for 2 hrs.	245	0·88	—	13	2·34	0·114
(*f*) As (*e*) for 4 hrs.......	353	1·87	—	21	4·20	0·220
(*g*) As (*e*) for 6 hrs. ...	437	2·00	—	49	5·18	0·297
(*h*) As (*e*) + 1% $PbEt_4$	218	0·38	—	9	0·14	0·016
(*i*) As (*f*) + 1% $PbEt_4$	238	0·50	—	13	0·29	0·049
(*j*) As (*g*) + 1% $PbEt_4$	265	0·68	—	19	0·99	0·099

* Determined at 70° F. in a No. 1 Redwood viscometer.

dry oxygen, and hexane was introduced. To the neck of the bulb was attached a tube containing phosphorus pentoxide, and the apparatus was fitted up and allowed to remain for 2 weeks, after which the pentoxide tube was sealed off and a reading taken. It was found that up to 275° there was only a very small rise of pressure above the normal curve, equal to about 10% of that usually occurring.

Contents of Bulb after Heating.—Qualitative tests only have been carried out, and in view of the work recently published by Callendar (*loc. cit.*), the project of quantitative work was abandoned. After being cooled, the contents of the bulbs possessed a peculiar penetrating smell, somewhat resembling that of a terpene. Water (even at temperatures just above the *C.I.T.*), aldehydes, acids, and oxides of carbon were detected, but no peroxides. In the case of all paraffins, however, a certain amount of gum was formed, light yellow for moderate temperatures, black for high temperatures. It was necessary to ascertain if these gums were produced during the process of heating, or if they were formed on cooling. Two test-tubes containing small quantities of octane were heated in a glycerol-bath to 250°, one tube being completely immersed, and the other partially. A brownish gum was observed on the exposed, and hence, cooler, part of the latter tube, whilst the other tube was clear when removed from the bath, but on subsequent cooling the condensed liquid was of a pale yellow colour. It is assumed that the gums are condensation products of the aldehydes which have been produced at the higher temperatures. Further, when any bulb containing paraffin hydrocarbon is heated above the *C.I.T.* and cooled, there is a fall of pressure, and after reheating, the derived pressure–temperature curve is lower than the first.

Comparative Results for Paraffin Hydrocarbons.—Since the temperature at which initial oxidation occurs is dependent on various factors, a series of experiments was arranged so that conditions were more comparable, and the following details were taken into consideration : (1) The bulbs were of the same material and volume; (2) the rates of heating were identical as far as possible; and (3) the hydrocarbon vapours were in equimolecular proportion.

In Table V are the *C.I.T.*'s of several hydrocarbons of the paraffin series determined under these constant conditions, and also other data appertaining to them. An unsuccessful attempt has been made to discover some physicochemical significance of this initial oxidation temperature, but graphical methods show no linear relationship between these temperatures and boiling point, spontaneous-ignition temperature, heat of formation, or flash-point. The following conclusions, however, are drawn from these figures :

(i) The *C.I.T.* is lowered by increase of molecular weight.

(ii) The temperature for normal hydrocarbons may be below that of the isomerides.

(iii) There is a general parallelism between the *C.I.T.*'s and spontaneous-ignition temperature, both decreasing with rise of molecular weight.

(iv) The flash-point is lowered, whilst the *C.I.T.* is raised, when the molecular weight decreases.

TABLE V.

Hydrocarbon.	Mol. wt.	B. p.	*C.I.T.*	Spontaneous-ignition temp. in oxygen.
n-Pentane	72	36°	255°	476° (560—570° in air).
*iso*Pentane	72	28	263	—
n-Hexane	86	69	230	285°, 288°.
n-Heptane	100	97·5	209	298° (impure), 281°.
n-Octane	114	125	197	—
Nonane (impure)	128	150	193	—

The Mechanism of the Reaction and its Bearing on Detonation.

Two theories have been advanced to explain the primary action of oxidation of paraffin hydrocarbons : the older hydroxyl theory of Bone, and the recently advocated " peroxide " theory of Callendar (*vide supra*). The latter theory possesses no advantage over the former, and differs from it merely in postulating the interposition of two oxygen atoms in place of one between a C–H or C–C linkage. It is true that peroxides have been detected by passing vapour–air mixture through heated tubes and suddenly cooling the products, the effective yield being increased when the experiment was carried out with droplets, but the experiments of Callendar are inconclusive in that they do not show definitely that the peroxides are alkyl or dialkyl peroxides and not hydrogen peroxide. Even if the former are present they may be the result of secondary oxidation of unsaturated hydrocarbons previously produced, for these substances have been proved to yield peroxides readily. Moreover, there is the difficulty that the volume (or number of molecules) increases at the temperature of initial oxidation to the extent of 15—20% of the number of hydrocarbon molecules present. Peroxide formation can only occur with decrease in the number of molecules, and a simple peroxide decomposition cannot increase the final number of molecules. The pressure–temperature curves given on p. 1559 indicate a sharp rise in the number of molecules at the *C.I.T.*, followed by a small decrease in pressure below the normal curve, indicating chemical change occurring with decrease in the number of molecules.

Stability of Paraffin Hydrocarbons.—This depends on the molecular weight and configuration of the molecule. In accordance with the researches of Berthelot, the effect of heat may be summarised in the reversible reactions

(i) $C_nH_{2n+2} \rightleftarrows C_nH_{2n} + H_2$ (lower temperatures).
(ii) $C_nH_{2n+2} \rightleftarrows C_{n/2}H_n + C_{n/2}H_{n+2}$ (higher temperatures).

Many objections have been raised against this theory of a state of equilibrium, and in actual practice several side reactions may be concurrent, especially at higher temperatures. At 300—400°, however, there is an undoubted production of hydrogen, but this is always accompanied by molecular changes.

A priori reasoning might lead one to conclude that with increasing hydrogen–carbon ratio the former element would split off more easily. Such, however, is not the case, and methane, with its higher proportion of hydrogen, is more stable than any member of the series. For hydrocarbons of this series, the heat of formation may be taken as a measure of the mean stability of the carbon atoms in the molecule. The molecular heat of formation increases with the number of carbon atoms present, but the heat of formation per carbon atom diminishes as shown by Thomsen's results :

Hydrocarbon.	Heat of formation (constant volume).	Mean heat of formation per carbon atom.
Methane (CH_4)	+16·5 Cals.	16·5 Cals.
Ethane (C_2H_6)	22·1	11·05
Propane (C_3H_8)	25·4	8·46
Butane (C_4H_{10})	29·1	7·27
Pentane (C_5H_{12})	1·5	6·30

The same investigator has shown that the average thermal values of the C–C and C–H linkages are approximately the same, so that Mean heat of formation/Valency of carbon may be taken as a relative measure of each valency attraction. There is no experimental justification for assuming that in a given molecule the forces of attraction of the C–C and C–H linkages are equal, and evidence is in favour of the view that there are some hydrogen atoms which are more easily split off than others. Besides the position of the hydrogen atoms and molecular weight, isomerism will be a contributing factor to the ease or otherwise of splitting off the hydrogen atoms.

A comparison of hydrocarbons of the different series presents more difficulty in that the naphthenes and aromatics contain ring compounds, but for those members containing the same number of carbon atoms, *viz.*, hexane, *cyclo*hexane, and benzene, the proportion of hydrogen and heat of formation decrease in the order given, whilst it seems probable, from the scanty data available, that the ease with which hydrogen is split off is greatest for that molecule containing the highest ratio of hydrogen atoms to carbon atoms, the latter being constant in each series.

Primary Dehydrogenation Theory.—The view held, as the result of the experimental work, is that primary oxidation consists in the direct combination of oxygen with those atoms of hydrogen which are most easily split off from the hydrocarbon molecule, the initial products being unsaturated hydrocarbons, containing one or more double bonds, and water. This will account for (*a*) the increase in the number of molecules at the *C.I.T.*, *e.g.*, $2C_2H_6 + O_2 \longrightarrow 2C_2H_4 + 2H_2O$; (*b*) the high percentage of water in the products formed above the *C.I.T.*, this percentage being only slightly increased at considerably higher temperatures; and (*c*) the appreciable proportion of unsaturated hydrocarbons formed near the *C.I.T.*

Secondary reactions ensue, the oxygen combining with the unsaturated hydrocarbons to produce aldehydes, peroxides, etc. This reaction reveals itself in the slight fall in the pressure–temperature curves just above the *C.I.T.* Striking confirmation of this was obtained by heating amylene–air as in the above experiments : an actual depression in the curve occurred, commencing at 232° and continuing up to 254°, after which a gradual rise above the theoretical curve followed. No water was detected in the finally cooled products; but considerable gum formation had taken place.

From the foregoing statements on stability it would appear that methane is the most stable of the hydrocarbons towards oxygen. This is actually the case and it must be observed that the difficulty of oxidation is increased by the probability that two hydrogen atoms must be removed from one carbon atom to form water, leaving CH_2 residues, which react eventually in various ways. Ethane is far less stable and one hydrogen atom may be removed from each of two adjacent carbon atoms to yield a double bond. Similarly, the higher hydrocarbons can give rise to conjugated double bonds which will enter vigorously into secondary oxidations. In the two cases which have been studied, the normal hydrocarbons appear to be more active than the isomerides. If this statement is of general validity, it may be that the isomeride with the fewest carbon atoms in the main chain is most stable, or that side chains retard removal of hydrogen atoms, or that two or more hydrogen atoms attached to adjacent carbon atoms are more readily oxidised.

Thermal Value of the Dehydrogenation.—The removal of hydrogen with formation of water will be exothermic, and the elimination of only two hydrogen atoms from heptane will produce considerable heat :

$$C_7H_{16} + O = C_7H_{14} + H_2O + 38 \text{ Cals.}$$

These two factors, *viz.*, (*a*) increase in number of molecules, and (*b*) production of heat, must play a considerable part in the detonation of hydrocarbons in petrol engines. The former increases the maximum pressure attained slightly above that calculated from the compression ratio, whilst the second factor may under suitable conditions raise the temperature above that of spontaneous ignition, thus giving rise to pre-ignition. During the slow heating of these hydrocarbon–air or oxygen mixtures, the heat of the initial reactions is dissipated by conduction and radiation, and it has been shown (Callendar) that under such conditions the mixture can be heated to temperatures above 650° without explosion. This is not the case, however, for sudden heating by compression, and, on the assumption that this takes place adiabatically, the theoretical rise in temperature above that resulting from compression alone may be calculated. For a 10% heptane–air mixture, if only two hydrogen atoms are removed from the molecule to produce water, and if the high value of 0·5 cal. is taken as the specific heat of heptane (liquid), the rise in temperature due to primary dehydrogenation alone is calculated to be more than 400°. A final temperature of about 370° is obtained by a compression ratio of 3 : 1, so a theoretical maximum of at least 770° is possible. The high value for the specific heat of heptane is used because it has been shown that condensation of these vapours can occur during compression.

This factor must be considered in the question of detonation. In internal combustion engines, to the heat of compression must be added the heat liberated by primary dehydrogenation, which must considerably raise both the pressure and the temperature of the mass of vapours. The increase in the number of molecules above the *C.I.T.* will also contribute to a rise in pressure. Primary dehydrogenation must then be the main cause of pre-ignition and detonation, and the ease of detonation increases with the hydrogen ratio. It is significant that the unsaturated hydrocarbons are more unstable and possess lower ignition temperatures than the paraffins, yet the latter detonate more easily. The reason is that the temperatures attained by equal compressions are far from comparable. Any factors, therefore, which will reduce the amount of heat liberated by primary dehydrogenation will diminish the tendency to detonation and allow of higher compressions. They may include reduction of paraffins, especially those of high molecular weight, dilution, negative catalysts, or a preliminary slow heating to a temperature above the *C.I.T.* Moreover, at higher speeds of the engine, the time may be too small to allow of completion of the chemical reactions involved at the *C.I.T.*

Action of Metallic Catalysts.—These are divided into two groups : (*a*) promoters of detonation; (*b*) " antiknocks." They have been classified also as positive and negative catalysts, and there is some apparent connexion between the ease of oxidation and oxide stability, and their catalytic action. The antiknock metals promote the combination of hydrogen and unsaturated hydrocarbons at low temperatures, and it is now suggested that their action as antiknocks depends upon the complete or partial prevention of dehydrogenation with its attendant water and heat formation, thus reducing the final temperature at the end of the compression stroke. From what has been said, it may be concluded that positive catalysts, *e.g.*, platinum, promote the reaction $H_2 + O \longrightarrow H_2O$, and that lead tetraethyl inhibits this change or even poisons the direct action of oxygen on the hydrocarbon, but there is no doubt that the amount of water formed is either nil or almost negligible.

The Action of Unsaturated Hydrocarbons and Aromatics.—These hydrocarbons have an appreciable effect in lowering the detonating qualities of a petrol, but large percentages must be present. It is well known, for example, that " cracked spirit " can be subjected to higher compression ratios than straight spirit, and this raises an objection to the peroxide theory of Callendar. Cracked spirit contains unsaturated hydrocarbons of the olefin type and also dienes even after refining; these are essentially peroxide-forming, and should increase rather than decrease detonation. It is suggested, therefore, that these hydrocarbons are effective as antiknocks in that they (*a*) have a smaller hydrogen content and are less likely to be dehydrogenated, *i.e.*, they act partially as diluents; and (*b*) they may enter into combination with the hydrogen evolved from the paraffins, by increasing the active mass of unsaturated hydrocarbons. Thus in the reaction $C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2$, the olefins produced are reinforced by the unsaturated hydrocarbons of the petrol, and even of the aromatics, and so tend to reverse the reaction with a decrease in the active mass of hydrogen. These unsaturated hydrocarbons are reducing agents. Benzene itself has a tendency to combine with hydrogen at low temperatures. In view of the nature of unsaturated hydrocarbons, their instability, and their tendency to form peroxides, their behaviour in an engine is contrary to expectation; the above may be the real explanation of the facts, and perhaps secondary oxidation products, such as aldehydes, peroxides, etc., are practically negligible on account of the time factor.

The Action of Aromatic Amines.—Any substance that combines with hydrogen under conditions prevailing in the engine, *i.e.*, that competes with oxygen for the hydrogen split off from the hydrocarbons, will tend to decrease detonation. The action of substances such as aromatic amines may be due in small part to dilution, but chiefly to the fact that they undergo decomposition, leaving residues which can unite with hydrogen. In the simplest case, aniline, the possible changes are

$$\text{(i)}\quad C_6H_5{\cdot}NH_2 = C_6H_5{\cdot} + {\cdot}NH_2,$$
$$\text{(ii)}\quad C_6H_5{\cdot} + {\cdot}NH_2 + 2H = C_6H_6 + NH_3.$$

The effectiveness of such reagents will therefore depend on (*a*) their concentration, (*b*) the ease (or temperature) of decomposition, and (*c*) the thermal action with hydrogen, which should be as small as possible and preferably endothermic.

The action of iodine is capable of some similar explanation, and it is noteworthy that, unlike iodine, bromine and chlorine are slight "knock" inducers; moreover, it is suggestive that their compounds with hydrogen are exothermic, whereas hydrogen iodide is endothermic. Finally, there is the suggestion contained in the above that the ethyl groups from the decomposition of lead tetraethyl increase its efficiency by reducing the effective mass of hydrogen.

Ignition of the Liquid Phase.—The published results of ignition temperatures are far from concordant even when determined by similar methods, and the two factors already discussed, *viz.*, increase of volume at the *C.I.T.* and the exothermic nature of this change, must be considered in methods based upon compression. Moore's method (*J. Soc. Chem. Ind.*, 1917, **36**, 109) consists in allowing drops of the liquid to fall on a hot platinum dish containing oxygen. The liquid phase, however, is less stable than the vapour (see above), and the results are lower than those obtained by the compression method. Doubtless, too, the size of the droplet and the catalytic effect of the surface play an important part, and this subject is reserved for a future paper. It might be argued that the ignition point of the liquid phase is lower on account of the adsorption of peroxides by the liquid, according to the views of Callendar, but it is known that peroxides do not affect the ignition temperature to any appreciable extent. This constitutes a serious objection to the peroxide theory. According to the views elaborated in this paper, the greater instability of paraffin droplets is due to the great concentration of molecules in the neighbourhood of the drop, with the attendant increase of chemical activity near the surface, and to the fact that the liquid phase absorbs far more heat than the vapour. Thus some of the heat of primary dehydrogenation may be used in suddenly heating the hydrocarbon above its ignition temperature.

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

[*Received, March* 29*th*, 1927.]