The Combustion of Hydrocarbons.

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I. INTRODUCTION.

MY purpose is threefold : to direct attention to the more outstanding facts of hydrocarbon combustion, to demonstrate some of them experimentally, and to outline a theory accounting for them. It is a subject not only of theoretical interest but also of great practical importance, for we depend on hydrocarbon–air explosions for much of our daily locomotion, whether by land, water, or air—and have still a deal to learn about them. Having studied them for upwards of 40 years, I have discovered at least their complexity, and wonder how some of the current notions concerning them originated. Anyway, I scarcely need apologise for relating the story of their scientific investigation during the past half-century.

At its commencement the notion of a preferential burning of hydrogen in hydrocarbon combustion generally prevailed, notwithstanding its inconsistence with discoveries first made, as long ago as 1803—4, by John Dalton in regard to explosions of methane and ethylene each with its own volume of oxygen. He had found that in neither case was any carbon liberated, and that with ethylene there was an immediate production of carbonic oxide and hydrogen, without any separation of carbon or appreciable steam formation, thus : $C_2H_4 + O_2 = 2CO + 2H_2$. The truth, thus so clearly revealed, was soon buried under accumulating errors, until, eighty years later, in his Cantor Lectures on the " Uses of Coal-gas " at the Royal Society of Arts, H. B. Dixon, whose star was then just appearing on the horizon of Oxford, endorsed the then prevalent view that " *ethylene when raised to a high temperature in contact with air is decomposed, the hydrogen burning first and the carbon afterwards.*"

The whirligig of time, however, soon brought its revenges when, seven years later, in Dixon's own laboratory in Manchester, the truth was re-discovered. And we may appropriately begin our demonstrations by repeating the experiment as it was then actually performed, as follows :—

Experiment. A mixture containing $C_2H_4 = 49{\cdot}4$, $O_2 = 47{\cdot}7$, and $N_2 = 2{\cdot}9\%$ was fired in a leaden coil at an initial pressure (p_1) of 756 mm.; the resulting explosion was violent, and the cold products were found to be under a pressure (p_2) of 1503 mm., or practically double that of the original mixture ($p_2/p_1 = 1{\cdot}988$).* They burned with a bluish flame, and on subsequent analysis were found to be composed of substantially equal volumes of carbonic oxide and hydrogen, as follows : $CO_2 = 0{\cdot}35$, $CO = 49{\cdot}1$, $H_2 = 48{\cdot}8$, $CH_4 = 1{\cdot}0\%$, as represented by the equation $C_2H_4 + O_2 = 2CO + 2H_2$ (Bone and Lean, J., 1892, **61**, 873). Soon afterwards it was also found that an equimolecular mixture of acetylene and oxygen behaves similarly on explosion, in accordance with the equation $C_2H_2 + O_2 = 2CO + H_2$, the volume in this case being increased by one-half.

Dixon directed attention to these results in his Bakerian Lecture of 1893 (*Phil. Trans.*, 1893, *A*, **184**, 161), in which he also dealt with the rates of explosion (*i.e.*, detonation)—in metres per sec. at 10° and 760 mm.—of methane, ethylene, and acetylene, each with oxygen in varying proportions between the equimolecular and those required for complete combustion, which he had found were as follows :—

$CH_4 + O_2$ 2528	$CH_4 + 1\frac{1}{2}O_2$ 2470	$CH_4 + 2O_2$ 2322
$C_2H_4 + O_2$ 2507	$C_2H_4 + 2O_2$ 2581	$C_2H_4 + 3O_2$ 2368
$C_2H_2 + O_2$ 2961	$C_2H_2 + 1\frac{1}{2}O_2$ 2716	$C_2H_2 + 2\frac{1}{2}O_2$ 2391

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* In this and all similar connections throughout this memoir, p_1 = initial firing pressure and p_2 = pressure of the cold products of an explosion.

And he inferred therefrom that in the wave itself the carbon burns to the monoxide, its further oxidation always being an after-occurrence.

It was during 1891—2, while such experiments were in progress, that I began assisting Dixon; and in conjunction first with B. Lean and afterwards with the late J. C. Cain, I studied the behaviours of both ethylene and acetylene on explosion with less than equimolecular proportions of oxygen, with results which were published in the Society's Journal (1892, **61**, 873; 1897, **71**, 26).

About this time, also, Smithells and Ingle discovered large quantities of hydrogen and carbonic oxide in the interconal gases of aërated hydrocarbon flames; and we are now repeating their separation of the two cones of an ethylene–air flame, showing an inner greenish-blue cone, and an outer lilac-blue cone, without any separation of carbon, the composition of the interconal gases being given by Smithells and Ingle as $CO_2 = 3{\cdot}6$, $CO = 15{\cdot}6$, $C_nH_m = 1{\cdot}3$, $H_2 = 9{\cdot}4$, $H_2O = 9{\cdot}5$, and $N_2 = 60{\cdot}6\%$. From this the authors concluded that "*when the hydrocarbon first burns in the inner cone there is a distribution of the limited supply of oxygen between the carbon and hydrogen, such that either carbon monoxide, water, and hydrogen are first formed,*" this being followed by the reversible water-gas

$$CO + OH_2 \rightleftharpoons CO_2 + H_2$$

reaction as the medium cooled down (J., 1892, **61**, 214).

As the outcome of all these experiments, the dogma of the preferential combustion of hydrogen was finally overthrown; and in its place was revived the opposite idea, originally put forward by Kersten in 1861, that in hydrocarbon flames generally "*before any part of the hydrogen is burnt all the carbon is burnt to carbonic oxide.*"

This was, however, strongly opposed by H. E. Armstrong, and during the nineties of last century the arena witnessed many resounding passages of arms between the various protagonists—for (mark you) those were real Victorian fighting days, when skins were thicker than now and hard blows were gaily exchanged. I watched with admiration the sword-play of my seniors, aiming a blow myself as opportunity arose, for I was not then the ardent pacifist I have since become. The fight swayed to and fro for years, but at length died down with honours easy; eventually, however, the revived doctrine of a preferential combustion of carbon, round which the fight had chiefly raged, was overborne as new facts emerged, and therefore had to be abandoned.

As far back as 1874, however, H. E. Armstrong had suggested another alternative —namely, that the successive stages in the burning of hydrocarbons involve the transient formation of unstable hydroxylated molecules which, according to circumstances, would decompose more or less rapidly under the influence of heat, giving rise to simpler intermediate products so that the process might be visualised as essentially one of "hydroxylation." But no attempt had been made to explore it experimentally, though it has ultimately proved a key to the problem.

At this point I would stress the importance of our viewing the subject widely, because what is most needed to-day is a balanced judgment embracing the whole range of conditions from those of slow combustion right up through flame and explosion under high pressure to detonation, all of which have been studied in my laboratories, and, in what follows, I shall endeavour to summarise our experiences and to give you my considered view regarding their interpretation as a whole.

II. SOME GENERAL CONSIDERATIONS.

Save in one or two isolated instances, up to almost the end of last century the investigation had been confined to flame and explosions, and practically nothing was known about the slow combustion of hydrocarbons. Yet obviously, if unstable oxygenated molecules of any kind are initially formed, the chance of detecting and isolating them would be far greater in slow than in explosive combustion. Hence in 1898 I commenced at Manchester University a systematic investigation of the matter which after 35 years is now nearing completion in my laboratories at the Imperial College, South Kensington.

Before, however, dealing with this part of the evidence, it may be recalled how it has been found (i) that suitably proportioned hydrocarbon–oxygen mixtures react with measurable velocities at temperatures much below those required for any appreciable reaction in such media as $2H_2 + O_2$, $2CO + O_2$ (moist), $CO + OH_2$, $CO_2 + H_2$, etc.; (ii) that such slow combustions are always preceded by a definite "induction period," the duration of which depends upon temperature and pressure; and (iii) that they do not require the presence of water vapour.

III. EVIDENCE FROM SLOW COMBUSTION AND THE DEVELOPMENT OF THE HYDROXYLATION THEORY.

Without describing the new experimental method and technique, including those for high-pressure conditions, developed during our researches in this part of the field, I will now briefly outline the principal results that have accrued therefrom to date.*

So far the experiments have been mainly concerned with interactions of oxygen in various proportions with the simpler aliphatic hydrocarbons methane, ethane, ethylene and acetylene, although some on propane have been included and progress has been made with the investigation of benzene and toluene. Temperatures have ranged between 250° and 400°, and pressures from under atmospheric up to about 100 atmospheres.

With regard to the four simpler aliphatic hydrocarbons, it has now been definitely established: (i) that after an "induction period," the duration of which depends on temperature, pressure, and mixture composition, all undergo quiet flameless combustion producing alcohols, aldehydes, acids, steam and oxides of carbon, *without any appearance whatever of carbon or hydrogen*, in circumstances precluding any appreciable independent oxidation of either hydrogen or carbonic oxide; (ii) that methane is much less readily so oxidised than the other three; (iii) that the most reactive mixtures, in regard either to the shortness of the induction period or to the subsequent speed of oxidation, are those containing hydrocarbon and oxygen in the 2 : 1 (*i.e.*, the alcohol-forming) molecular proportion; (iv) that in *all* cases alcohol and/or aldehyde formation precedes that of oxides of carbon, while with acetylene there appears to be a transient formation of glyoxal, $C_2H_2O_2$, which immediately gives rise to carbonic oxide and formaldehyde before any steam appears; and (v) that in *all* cases, carbon dioxide is formed in circumstances which, while precluding its arising by the secondary oxidation of the monoxide, favour its doing so by the oxidation of formic acid, which is always present among the products. Point (iii) is well illustrated by a series of pressure–time curves (Fig. 1) observed with various ethylene–oxygen mixtures reacting at 300°.

The normal intermediate formation of the following alcohols, aldehydes or acids during the slow oxidations of the said hydrocarbons has now been definitely established:

(i) *Methane :* Methyl alcohol, formaldehyde, and formic acid.

(ii) *Ethane :* Ethyl and methyl alcohols, acet- and form-aldehydes, acetic and formic acids.

(iii) *Ethylene :* Vinyl alcohol and its isomerides ethylene oxide and acetaldehyde, formaldehyde, and formic acid.

(iv) *Acetylene :* Glyoxal, $C_2H_2O_2$, formaldehyde and formic acid.

And as regards the two aromatic hydrocarbons referred to, Dr. Newitt has recently proved an initial formation of phenol in the case of benzene and of benzyl alcohol, followed by that of benzaldehyde, in the case of toluene.†

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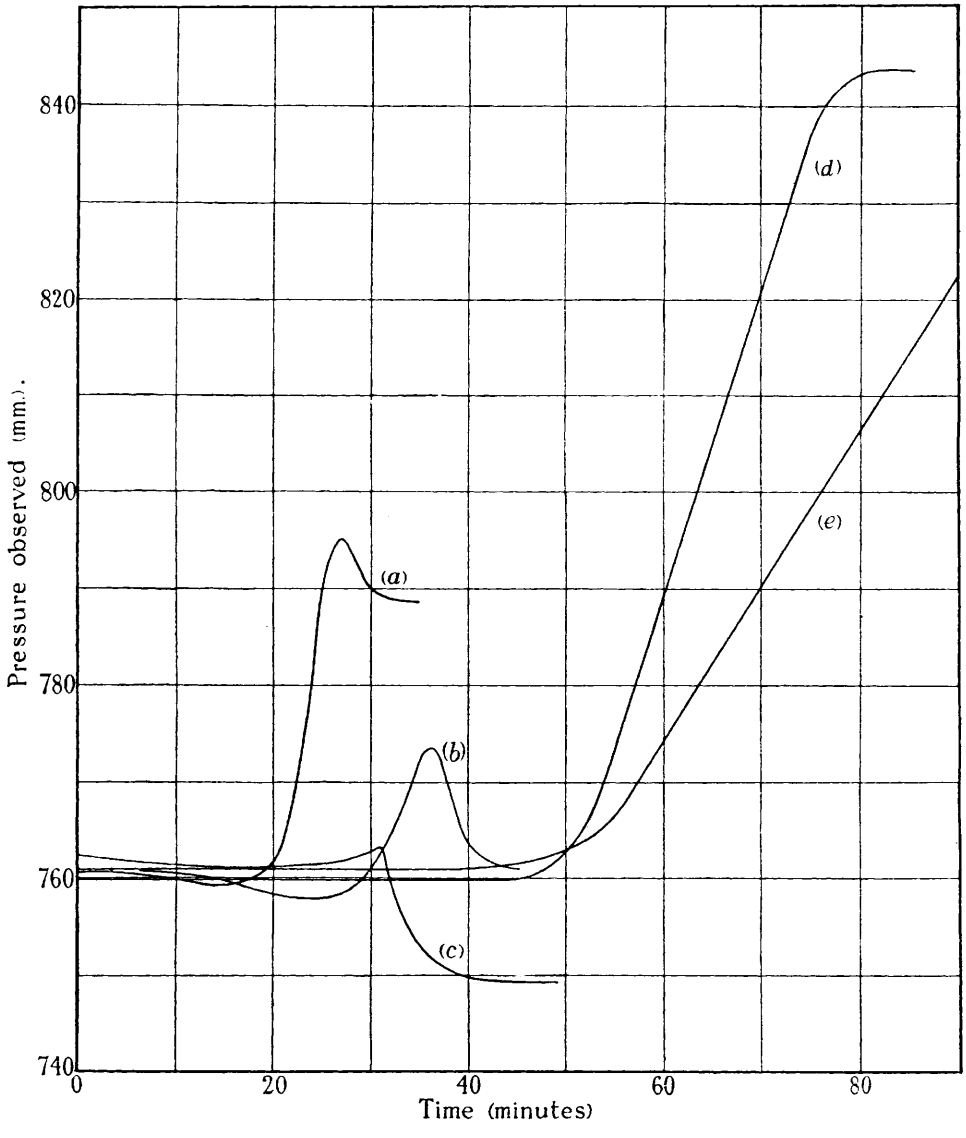
* My chief collaborators have been R. V. Wheeler, W. E. Stockings, G. W. Andrew, and J. Drugman in Manchester (J., 1902, **81**, 535; 1903, **83**, 1074; 1904, **85**, 693, 1637; 1905, **87**, 1232; 1906, **89**, 652, 939) and D. M. Newitt, R. E. Allum, S. G. Hill, A. E. Haffner, A. M. Bloch, and H. F. Rance in London (*Proc. Roy. Soc.*, 1929, *A*, **129**, 434; 1932, **134**, 578, 591; 1932, **137**, 243; 1933, **140**, 426, and another now in the press).

† Some historical points pertaining to the detection and isolation of intermediate products, having been dealt with in my recent Bakerian Lecture on the subject (*Proc. Roy. Soc.*, 1932, *A*, **137**, 243—274), are omitted now.

It should also be noted in passing that, although in favourable circumstances some "peroxidation" of intermediately produced aldehydes has been observed, no evidence has been forthcoming of any initial alkyl peroxide formation, a point to which we shall revert later.

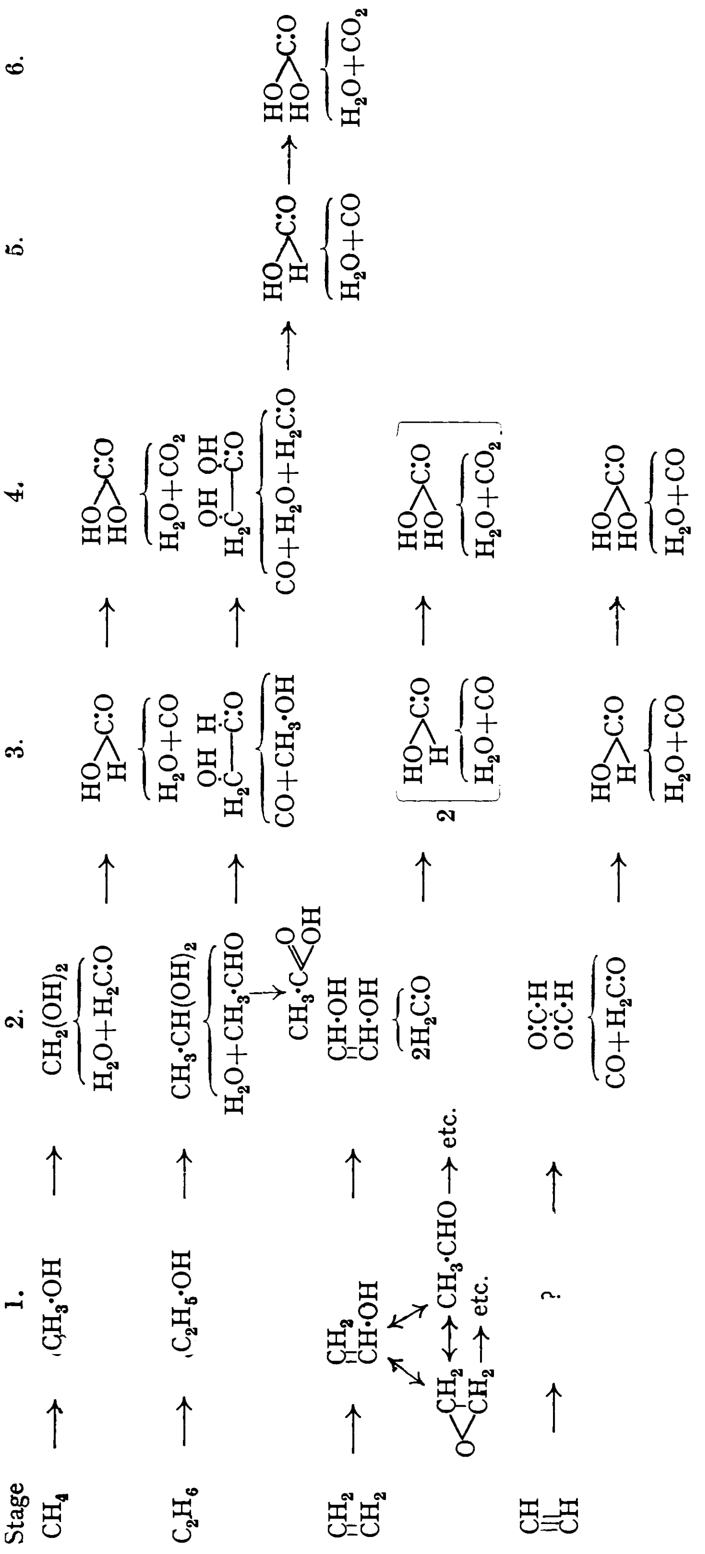
FIG. 1.

Observed pressure-time curves with various C_2H_4–O_2 *mixtures at* 300°, *namely*: (*a*) $2C_2H_4 + O_2$, (*b*) $3C_2H_4 + O_2$, (*c*) $5C_2H_4 + O_2$, (*d*) $C_2H_4 + O_2$, *and* (*e*) $C_2H_4 + 2O_2$.



General Course of Oxidation.—Viewing the evidence broadly, and as a whole, we visualise the slow oxidation of these hydrocarbons—subject to the proviso that, so far as the evidence at present available goes, with acetylene the first recognisable product would appear to be glyoxal—as involving throughout a series of successive hydroxylations and thermal decompositions, mainly as on p. 1603 :—

The Slow Oxidation of Hydrocarbons.



Although, when working at atmospheric pressure, it is difficult to isolate the initial monohydroxylated product (alcohol) in such cases—for, as we have found, under such conditions the newly-born alcohol is oxidised more rapidly than the original hydrocarbon *—pressure so favours its stability that usually in pressure-oxidations it can be isolated and quantitatively estimated. Thus, for example, employing a $8CH_4 + O_2$ mixture at 340° and a pressure of 106 atmospheres, Drs. D. M. Newitt and A. E. Haffner (*Proc. Roy. Soc.*, 1932, *A*, **134**, 591) found that 22·3% of the methane burnt survived as methyl alcohol in the products; while with a $9C_2H_6 + O_2$ medium at 273° and 100 atmospheres Newitt and Bloch (*ibid.*, 1933, *A*, **140**, 426) have recently obtained the following complete quantitative proof of the foregoing " hydroxylation " scheme for ethane:

Pressure-oxidation of ethane at 273° *and* 100 *atmospheres.*

Percentage of the carbon of the ethane burnt surviving in the product as:	Ethyl alcohol (Stage 1)	35·4
	Acetaldehyde (7·5) and acetic acid (3·8) (Stage 2)	11·3
	Methyl alcohol (18·2) and CO (18·2) (Stage 3)	36·4
	Formaldehyde (0·4) and CO (0·4) (Stage 4)	0·8
	Formic acid (0·4) and CO (3·0) (Stage 5)	3·4
	Carbonic anhydride (Stage 6)	13·1
		100·4

Such, I venture to think, is a remarkable experimental achievement of which its authors may be justly proud. Moreover, seeing (i) that each possible successive stage in the postulated " hydroxylation " scheme was verified by the isolation and estimation of the particular product (or products) involved, (ii) that the whole of the ethane burnt was thus accounted for, and (iii) that throughout the experiments no trace of " peroxide " was ever detected, such a result is of the highest significance.

We are also indebted to Newitt for another important new link in the chain of evidence. For during the past month or so he has succeeded in isolating vinyl alcohol—by means of its characteristic double compound (a granular white precipitate) with mercuric oxychloride †—from among the products of the pressure-oxidation of ethylene; and as its two isomerides, ethylene oxide and acetaldehyde, have also been isolated during the process, as well as in the slow oxidation of the hydrocarbon at atmospheric pressure, it seems now definitely established that the initial stage in the combustion is really one of " hydroxylation," followed by a rapid transition towards a triangular equilibrium, dependent on pressure and temperature, between the three isomeric forms of C_2H_4O, such that (as would now appear) at 300° and atmospheric pressure the equilibrium molecular ratio appears to be approximately 4 vinyl alcohol : 10 ethylene oxide : 1 acetaldehyde; increasing pressure favours the stabilities of vinyl alcohol and acetaldehyde at the expense of ethylene oxide.‡

The pressure-oxidation process having thus proved so effective in Newitt's hands in describing the initial hydroxylation product in the cases of methane, ethane, and ethylene, it may be hoped that he will apply it to acetylene also, with a view to clearing up the obscurity still veiling the initial stage of its oxidation.

Summary.—This part of the evidence may, I think, be fairly summed up by saying, in regard to the slow oxidation of the hydrocarbons so far investigated by us in detail (*i.e.*, methane, ethane, ethylene, and acetylene): (i) that in each case the most reactive hydrocarbon : oxygen ratio is 2 : 1, and—save with acetylene, where there is still some obscurity—the first recognisable product is the corresponding alcohol; also with benzene it is phenol and with toluene benzyl alcohol; (ii) that, subject to the said qualification as

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* It should, however, be noted that as long ago as 1906 J. Drugman, working with me in Manchester, showed that, on oxidation with ozone at 100°, ethane yields successively ethyl alcohol, acetaldehyde, and acetic acid (J., 1896, **89**, 939).

† This test for vinyl alcohol in aqueous solution is due to Poleck and Thümmel (*Ber.*, 1889, **22**, 2863), who found the reaction to be : $H_2C{:}CH{\cdot}OH + HgOCl,HgCl_2 = H_2C{:}CH{\cdot}O{\cdot}HgO,HgCl_2 + HCl$.

‡ As, however, the investigation of this aspect of the matter is still proceeding in our laboratories at South Kensington, further discussion of it must be reserved for a future publication.

regards acetylene, the hydroxylation theory, as outlined herein, has been substantiated by the isolation in quantity of every postulated intermediate product (or, when too unstable, then of the products of its thermal decomposition) ; (iii) that in each case (save acetylene) such products form a sequence corresponding with as many successive oxidation stages as there are atoms of hydrogen in the hydrocarbon molecule ; and (iv) that, apart from all such direct evidence, there is also the further outstanding fact that the hydrocarbon can be oxidised (*via* alcohols, aldehydes, and acids) ultimately to oxides of carbon and steam *without any liberation of either carbon or hydrogen*, a circumstance which, while eloquent of successive hydroxylations and thermal decompositions of hydroxylated molecules, can hardly be otherwise explained.

If the criterion of a scientific theory is its consonance with well-established facts rather than its speculative glamour, I am well content to leave mine so, not knowing what stronger proof of it could reasonably be required.

IV. Extension of the Theory to Explosive Combustion.

(1) *General Considerations.*—Although the conditions prevailing in hydrocarbon flames and explosions are obviously much more complex than those of slow combustion, the experimental evidence has convinced me that the result of the initial encounters between hydrocarbon and oxygen is the same in both, namely, the formation of an " oxygenated " (and usually a " hydroxylated ") molecule. Undoubtedly at the higher temperatures of flames, secondary thermal decompositions come into play at an earlier stage, and play a more conspicuous rôle, than in slow combustion ; there are, however, the strongest reasons for believing that they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence thereof. Moreover, on both thermochemical and kinetic grounds, it seems probable that in explosive combustion, whenever the oxygen supply suffices, there will be (so to speak) a " non-stop " run through the *monohydroxy-* to the *dihydroxy*-stage before thermal decomposition occurs ; albeit, in default of such oxygen-sufficiency, more or less decomposition at the monohydroxy-stage would probably occur, and in still greater oxygen-deficiency some of the excess hydrocarbon might also be decomposed.

In view of the complexities of flames, and of the great difficulties in tracking by chemical analysis the course of events therein, the utmost that can be reasonably required of any acceptable theory about them is that it shall be consistent with facts, provide a rational view thereof, and in a general way enable the main happenings in a particular case to be predicted. It can scarcely be expected that in *all* circumstances *all* the combustible molecules will be attacked by the oxygen in precisely the same way, for no such uniformity seems possible, and in special circumstances abnormalities may arise.

What we are now concerned with, however, are the normal occurrences, and I will endeavour to demonstrate some of the more outstanding features of the explosive combustion of hydrocarbons and how they fall into line with, and can be explained by, the theory as already outlined.

(2) *Thermal Decompositions of Alcohols and Aldehydes.*—Before doing so, however, I must say something about how the various oxygenated molecules intermediately formed during slow combustion would, or might, be thermally decomposed in flames. Fortunately, information is available concerning the effects of heat upon some of them, though in places it is incomplete. Moreover, with one or two exceptions, the mode of decomposition of such compounds varies with temperature, and therefore it is well to remember that there are wide differences in the mean temperatures of flames, especially according as the composition of the explosive medium concerned is near to one or other of the limits of inflammability or far removed from both of them.

Alcohols. At fairly low temperatures the vapours of primary alcohols decompose primarily into steam and an unsaturated hydrocarbon molecule or residue, but at higher temperatures into hydrogen and the corresponding aldehydes. In intermediate ranges both changes may occur simultaneously, and in flames they are always followed by secondary decompositions and/or hydrogenations, according to circumstances. Thus, for example, we might have :—

$CH_3{\cdot}OH$ primarily resolved into (i) $H_2C\colon + H_2O$ and/or (ii) $H_2C{:}O + H_2$ (— 9·3 kg.-cals.), followed by secondary resolutions of the $H_2C\colon$ residues ultimately into $C + H_2$, and of the $H_2C{:}O$ into $H_2 + CO$ (*vide* formaldehyde), and (in favourable circumstances) by hydrogenations of $H_2C\colon$ residues to CH_4.

$C_2H_5{\cdot}OH$ primarily resolved into (i) $C_2H_4 + H_2O$ (+ 7 kg.-cals.) and/or (ii) $H_2 + CH_3{\cdot}CHO$ (— 10 kg.-cals.), followed by secondary resolutions of C_2H_4 into $C_2H_2 + H_2$ and/or $2C + 2H_2$, and of $CH_3{\cdot}CHO$ into $CH_4 + CO$ and/or $C + 2H_2 + CO$ (*vide* acetaldehyde).

Aldehydes. At temperatures between about 400° and 600° (or thereabouts) aldehyde vapours containing one CHO group and one or more other carbon atoms are primarily resolved into CO and a saturated hydrocarbon; thus with *acetaldehyde* :—

(i) $CH_3{\cdot}CHO = CH_4 + CO$ . . . + 2 kg.-cals.

With further rising temperature, the breakdown becomes progressively more complete, tending at very high temperatures to some such final stage as

(ii) $CH_3{\cdot}CHO = C + 2H_2 + CO$ [*] . . . — 19·8 kg.-cals.

Formaldehyde. It is important to note (i) that of all the oxygenated molecules known to be formed in slow combustion, the vapour of formaldehyde is pre-eminently that which at *all* temperatures in flames decomposes primarily into carbonic oxide and hydrogen (*plus*, maybe, some trace of methane) without any separation of carbon whatever, thus :

$$H_2C{:}O = H_2 + CO \;.\;.\;. - 13{\cdot}5 \text{ kg.-cals.};$$

and (ii) that, since $H_2C{:}O$ is inherently a much more stable configuration than $H{\cdot}\overset{\bullet}{\underset{\bullet}{C}}{\cdot}OH$, it would readily be formed therefrom, an important consideration in connection with the partial combustion of olefins.

Glyoxal vapour probably would be resolved at *all* temperatures primarily into $CO + H_2C{:}O$ and secondarily into $2CO + H_2$, also without any carbon deposition, but precise knowledge is lacking.

Consequently, whenever the explosion of a hydrocarbon–oxygen mixture results in substantially nothing but carbonic oxide and hydrogen, without any carbon deposition, an intermediate formation of formaldehyde, or possibly glyoxal (or both), may reasonably be inferred.

(3) *The Relative Combustibilities of Hydrocarbons and Hydrogen* (*or Carbonic Oxide*).—The first general fact to note is that, as will be shown presently, the affinities of hydrocarbons so greatly exceed those of either hydrogen or carbonic oxide for oxygen that, in explosions of hydrocarbon–hydrogen (or carbonic oxide)–oxygen media where oxygen is very deficient, the hydrocarbon is burnt, as it were, preferentially. Moreover, the mutual affinity between oxygen and a hydrocarbon so overpowers any tendency for the latter to decompose thermally in flames that, whenever there is free oxygen at hand in the medium, a hydrocarbon molecule will combine with it rather than decompose. Hence the old notion, which still haunts chemical literature, of a hydrocarbon molecule normally undergoing thermal decomposition before oxidation in explosions should be abandoned. For such decomposition will only occur in regions where little or no oxygen is at hand for the hydrocarbon to react with. This being so, it is wrong to speak of the preferential combustion of either hydrogen or carbon in hydrocarbon flames; on the contrary, the hydrocarbon molecule, though it may have been " activated," is still intact when it seizes and incorporates the oxygen whether atomic or molecular.

Experiments. (*a*) To illustrate these points, I cannot do better than repeat a very striking experiment, first made in my laboratory in 1905, in which a mixture of acetylene

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[*] The whole sequence may perhaps be pictured as follows :

$$CH_3{\cdot}CHO \longrightarrow CH_4 + CO \longrightarrow {\cdot}CH_3 + H + CO$$
$$\longrightarrow {:}CH_2 + \left\{\begin{matrix}2H\\H_2\end{matrix}\right\} + CO \longrightarrow {\vdots}CH + \left\{\begin{matrix}3H\\H_2 + H\end{matrix}\right\} + CO \longrightarrow {:}C{:} + \left\{\begin{matrix}4H\\2H_2\end{matrix}\right\} + CO,$$

which would account for the spectrographic evidence of the presence of $\cdot CH_3$, $\colon CH_2$, $\colon CH$, and C_2 in such hydrocarbon flames; and so with other similar decompositions of alcohols, etc.

and electrolytic gas of the composition $C_2H_2 + O_2 + 2H_2$ was exploded in a sealed glass bulb at an initial pressure, p_1, of 534 mm.* The oxygen has here the opportunity of dividing itself between the hydrocarbon and the hydrogen, according to its relative affinities for them; and anyone, not knowing beforehand what actually happens, would probably predict some, and possibly a large, formation of steam as well as a resolution of part of the acetylene into its elements. Yet on firing the mixture, as you will see, a sharp bluish flame fills the vessel, but neither does carbon separate nor does any steam condense on cooling. In the experiment made in my laboratory, the pressure of the products in the bulb after the explosion, p_2, was 653 mm., the ratio p_2/p_1 being 1·22, and their percentage composition was

$$CO_2 = 0{\cdot}2,\ CO = 39{\cdot}8,\ CH_4 = 0{\cdot}2,\ \text{and}\ H_2 = 59{\cdot}8\%,†$$

showing that the whole of the original acetylene had been burnt to carbonic oxide and hydrogen, leaving the original hydrogen quite intact, in accordance with the equation $C_2H_2 + O_2 + 2H_2 = 2CO + 3H_2$.

Our recent photographic investigation of this explosion has shown its flame to be a very compact layer of incandescent gas, about 1 cm. in thickness, with a sharply defined front and no "after burning," the duration of luminosity being 1·6 millisecs. only. Indeed, we have found this to be the most *intensively* burning of all mixtures of acetylene and electrolytic gas, in the sense of both time and space concentration of the chemical change.

(*b*) Astonishing as such a result may appear, the proportion of hydrogen present may even be doubled without appreciably affecting it. Thus, for example, on firing a $C_2H_2 + O_2 + 4H_2$ mixture (actually containing $C_2H_2 = 16{\cdot}15$, $O_2 = 16{\cdot}05$, and $H_2 = 67{\cdot}80\%$) at $p_1 = 753$ mm. in my laboratory, there was again neither carbon deposited nor appreciable steam formation, the gaseous products ($p_2 = 850$ mm. and $p_2/p_1 = 1{\cdot}13$) containing

$$CO_2 = 0{\cdot}2,\ CO = 28{\cdot}1,\ H_2 = 70{\cdot}2,\ \text{and}\ CH_4 = 1{\cdot}5\%,†$$

i.e., corresponding very nearly with the equation $C_2H_2 + O_2 + 4H_2 = 2CO + 5H_2$. To illustrate this point, I will now similarly fire at atmospheric pressure (750 mm.) mixtures corresponding with $C_2H_2 + O_2 + 3H_2$ and $C_2H_2 + O_2 + 5H_2$, respectively. As you will see, in neither case is there any separation of carbon, and while in the first case no visible condensation occurs on cooling, in the second it is just discernible on close examination.

(*c*) To pursue the matter a little further, I will next show how little (if any) the $C_2H_2 + O_2 + 2H_2$ result (*a*) is affected by dilution with different so-called inert gases, by firing $C_2H_2 + O_2 + 2H_2 + 4(\text{He, Ar, or } N_2)$ mixtures at atmospheric pressure (750 mm.) each in a glass globe of about 350 c.c. capacity. It will be noticed that, while the colour of the explosion flame varies with the diluent, there is neither carbon separation nor any visible steam condensation with the helium- or argon-diluted media, although both are just discernible after the nitrogen-diluted explosion.‡ Clearly then, although the result may be slightly affected by nitrogen, lowering of the mean flame-temperature by such dilutions has not enabled the hydrogen to wrest any material proportion of the oxygen from the rapacious maw of the acetylene.

(*d*) To prove that such a result is not due to any peculiarity of acetylene, I will next similarly explode a mixture of ethylene, hydrogen, and oxygen of the composition $C_2H_4 + O_2 + H_2$ at an initial pressure, p_1, of 600 mm., when it will again be seen that neither does carbon separate nor does any steam condense on cooling. The pressure of the explosion products, p_2, will be *ca.* 900 mm. ($p_2/p_1 = 1{\cdot}49$) and their composition

$$CO_2 = 0{\cdot}35,\ CO = 39{\cdot}6,\ C_2H_2 = 1{\cdot}25,\ CH_4 = 3{\cdot}65,\ \text{and}\ H_2 = 55{\cdot}15\%,$$

showing that nearly the whole of the ethylene has been burnt to carbonic oxide and hydrogen, leaving the original hydrogen intact, as follows: $C_2H_4 + O_2 + H_2 = 2CO + 3H_2$.

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* Except as otherwise specifically stated, all the explosion experiments shown on the lecture table were carried out in cylindrical sealed glass bulbs 10 cm. long × 2·5 cm. diam. (capacity = *ca.* 80 c.c.), ignition being effected by an electric spark in the middle of the cylinder.

† The very small percentage of carbon dioxide in these products is in itself a proof of practically no steam having been formed during the explosions.

‡ These matters are reserved for further investigation.

(*e*) Much the same result is obtained, as will now be shown, by similarly exploding a mixture of propylene, hydrogen, and oxygen corresponding with the formula $C_3H_6 + 1\frac{1}{2}O_2 + H_2$. When the experiment was made in my laboratory at an initial pressure of $p_1 = 497$ mm., the whole of the carbon was accounted for in the gaseous products and only 10% of the original oxygen appeared as water, the details of experiment being as follows :—

$$p_1 = 497 \text{ mm.}, p_2 = 847{\cdot}8 \text{ mm.}, p_2/p_1 = 1{\cdot}705.$$

Gaseous products : $CO_2 = 1{\cdot}10$, $CO = 43{\cdot}5$, $C_nH_m = 0{\cdot}8$, $CH_4 = 2{\cdot}4$, and $H_2 = 52{\cdot}2\%$, or nearly corresponding with the equation :

$$C_3H_6 + 1{\cdot}5O_2 + H_2 = 3CO + 4H_2.$$

I would commend these experiments to my fellow-workers in the field as being of the highest significance in connection with the theory of explosive combustion generally. For, as Professor Armstrong has suggested (*J. Roy. Soc. Arts*, 1933, **81**, 567), at first sight it hardly seems a case of kinetics at all, but rather of ball-room tactics, oxygen molecules preferring the good-looking hydrocarbon and leaving the plainer hydrogen molecules as " wall-flowers," showing that there are more things in combustion than are yet dreamed of in our philosophies. Albeit, further experiments on $CH_4 + O_2 + xH_2$ and $C_2H_4 + O_2 + xH_2$ explosions at high pressures have shown that, in the long run, hydrogen does exert its mass-influence upon the oxygen-distribution.*

(4) *Evidence from Explosions of Methane, Ethane, Ethylene, or Acetylene with its own Volume of Oxygen.—Methane.* It has already been mentioned that on explosion with its own volume of oxygen—or just half that required for complete combustion—methane yields principally carbonic oxide, hydrogen, and steam, in conformity with the equation $CH_4 + O_2 = CO + H_2 + H_2O$, although some carbon dioxide is produced owing to the " water-gas reaction " $CO + OH_2 \rightleftharpoons CO_2 + H_2$ coming into play during the cooling period.

Experiment. This will be demonstrated by firing the mixture in a sealed glass bulb at an initial pressure of 730 mm. There is a sharp bluish flame without any separation of carbon, but steam is seen to condense on cooling. If time permitted an examination of the cold gaseous products, their pressure would be found to be about 750 mm. ($p_2/p_1 = 1{\cdot}027$) and their composition as follows :—

$$CO_2 = 6{\cdot}5,\ CO = 42{\cdot}0,\ H_2 = 50{\cdot}5, \text{ and } CH_4 = 1{\cdot}0\%.$$

Such result is just what might be predicted from the " hydroxylation " theory, supposing a " non-stop " run through the *monohydroxy-* to the *dihydroxy*-stage, followed immediately by a complete breakdown of formaldehyde into carbonic oxide and hydrogen and a subsequent " water-gas reaction " during the cooling, thus :

$$\begin{array}{l} CH_4 \longrightarrow CH_3{\cdot}OH \longrightarrow CH_2(OH)_2 \\ \qquad\qquad\qquad\qquad\quad \overbrace{H_2O + H_2{:}C{:}O} \\ \qquad\qquad\qquad\qquad\qquad\quad \overbrace{H_2 + CO}, \text{ and } CO + OH_2 \rightleftharpoons CO_2 + H_2 \end{array}$$

Although at atmospheric pressure methane–oxygen mixtures containing less than 40% of oxygen are non-explosive, yet by sufficiently raising the pressure they become so down to the $70CH_4/30O_2$ limit or thereabouts. My colleague, Dr. D. T. A. Townend, who has investigated the matter very thoroughly, found the results of their explosions to agree well with the theory, breakdowns occurring at both the mono- and di-hydroxy-stages (*Proc. Roy. Soc.*, 1927, *A*, **116**, 637).

Ethane. (*a*) " *Inflammation.*" The explosion of an equimolecular mixture of ethane and oxygen was immediately seen to be crucial as between the former idea of a preferential burning of the carbon and the " hydroxylation " theory. For, whereas, according to the former, only carbonic oxide and hydrogen should result, thus :—

$$C_2H_6 + O_2 = 2CO + 3H_2, \text{ with } p_2/p_1 = 2{\cdot}5,$$

---

* *Vide* Bone, Newitt, and Townend, "Gaseous Combustion at High Pressures," chap. XIX, pp. 300—308 (1929).

the " hydroxylation " theory would require the formation of methane, carbon, hydrogen, carbonic oxide; and steam, with some carbon deposition and a p_2/p_1 ratio materially less than 2·5 as follows :—

$$C_2H_6 \longrightarrow C_2H_5{\cdot}OH \longrightarrow \underbrace{CH_3{\cdot}CH(OH)_2}_{H_2O + \underbrace{CH_3{\cdot}CHO}_{\left\{\begin{matrix}CH_4 + CO\\ C + 2H_2 + CO\end{matrix}\right\}\ \textit{etc.}}}$$

Experiment. The experiment will now be repeated by firing a $C_2H_6 + O_2$ mixture in a sealed bulb at an initial pressure (p_1) of 730 mm. It will be observed that a lurid yellowish-red flame fills the vessel, accompanied by a black cloud of carbon particles; and a close inspection will reveal a considerable condensation of water also. If the bulb were opened, and rinsed out with water, the presence of aldehydic products could be demonstrated by means of Schiff's reagent. A detailed examination of the cold gaseous products would show their pressure to be some 50% greater than that of the original mixtures ($p_2/p_1 = 1{\cdot}5$) and their composition as follows :—

$$CO_2 = 4{\cdot}2,\ CO = 33{\cdot}5,\ C_nH_m = 2{\cdot}7,\ CH_4 = 11{\cdot}0, \text{ and } H_2 = 48{\cdot}6\%,$$

about one-sixth of the original carbon having been deposited as such. All this is in conformity with the hydroxylation theory.

It should be noted that in such an explosion the proportions of carbon separating during the reaction and of steam surviving in the products vary with the flame temperature and rate of cooling, both of which are influenced by the surface/volume ratio of the containing vessel. The smaller such ratio the hotter the flame and the slower the cooling, and, while the former favours carbon deposition, the latter allows of more " unburning " of the steam by carbon, $C + OH_2 = CO + H_2$. Indeed, both the separation of carbon and the formation of steam and oxides of carbon in hydrocarbon explosions are secondary effects in the sense that all result from thermal decompositions of the primary oxidation products.

Experiments showing effects of firing a $C_2H_6 + O_2$ *mixture in* (i) *a long tube and* (ii) *a globe of equal capacity.* This point may be illustrated by firing the equimolecular $C_2H_6 + O_2$ mixture in two glass vessels having approximately the same volume but widely different surface areas. For this purpose, (i) a closed tube about 100 cm. long and 2·5 cm. internal diameter, and (ii) a globe of 9·5 cm. internal diameter have been selected. Both these vessels have the same volume (*ca.* 500 c.c.) but the surface area of the tube is about 2·75 times greater than that of the globe. They have both been previously filled with the same $C_2H_6 + O_2$ mixture at a pressure of about 700 mm. On now comparing the results of the two explosions, as is done in Table I, it is at once evident that much more water and less carbon have survived in the tube than in the globe experiment. Indeed, the p_2/p_1 ratio is

TABLE I.

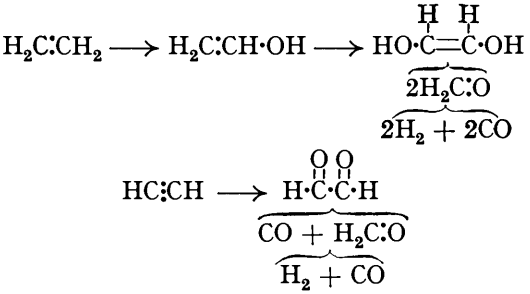
Inflammation of an Equimolecular Mixture of Ethane and Oxygen.

	(*a*). In long tube.			(*b*). In large globe.		
p_1, mm.	701			685		
p_2, mm.	1018			1187		
p_2/p_1	1·45			1·73		
Percentage composition of gaseous products : CO_2	4·20			3·40		
CO	34·80			36·10		
C_2H_2	5·00	7·65		0·15		
C_2H_4	2·65					
CH_4	8·85			7·25		
H_2	44·50			53·05		
C, H_2, and O_2 Balances.	C.	H_2.	O_2.	C.	H_2.	O_2.
Original mixture	694	1041	354	678	1017	346
Gaseous products	643	738	220	558	805	255
Difference (carbon, aldehyde, and H_2O)	51	303	134	120	212	91
Percentage difference	7·6	29	37·8	18	20	27·5

about 1·45 only in the former as compared with about 1·75 in the latter, and an examination of the products would show that the difference is accounted for by a much greater survival of steam, aldehydes, acetylene, and ethylene in the tube than in the globe experiment.

(*b*) *Detonation.* Had time permitted, it could be shown how the theory has been found to apply both to the "detonation" of $C_2H_6 + O_2$ mixtures and to their explosion in bombs at high pressures; but those interested may read the published evidence for themselves (J., 1906, **89**, 1620; *Phil. Trans.*, 1915, *A*, **215**, 310).

Ethylene and acetylene. The preferential burning of carbon which *apparently* occurs when either ethylene or acetylene is exploded with its own volume of oxygen, is just what would be predicted from the theory outlined herein as follows :—



$$H_2C{:}CH_2 \longrightarrow H_2C{:}CH{\cdot}OH \longrightarrow \underbrace{\underbrace{HO{\cdot}\overset{H}{C}{=}\overset{H}{C}{\cdot}OH}_{2H_2C{:}O}}_{2H_2 + 2CO}$$

$$HC{\vdots}CH \longrightarrow \underbrace{\underbrace{H{\cdot}\overset{O}{\overset{\|}{C}}{\cdot}\overset{O}{\overset{\|}{C}}{\cdot}H}_{CO + H_2C{:}O}}_{H_2 + CO}$$

Experiments. Each of these equimolecular mixtures (*a*) $C_2H_4 + O_2$ and (*b*) $C_2H_2 + O_2$ will now be fired in sealed bulbs at initial pressures (p_1) of about 500 and 300 mm. respectively. It will be seen that in neither case is there even the slightest separation of carbon or condensation of steam on cooling, which is in striking contrast with what happened in the corresponding $C_2H_6 + O_2$ explosion. An investigation of the cold products would reveal in each case a large increase in the pressure, namely, (*a*) almost a doubling in the ethylene and (*b*) by nearly 50% in the acetylene explosion, and their composition would be :—

(*a*) $CO_2 = 0{\cdot}5$, $CO = 50{\cdot}0$, $H_2 = 47{\cdot}5$, and $CH_4 = 2{\cdot}0\%$, with $p_2/p_1 = 1{\cdot}95$;

(*b*) $CO_2 = 0{\cdot}75$, $CO = 67{\cdot}0$, $H_2 = 30{\cdot}75$, and $CH_4 = 1{\cdot}5\%$, with $p_2/p_1 = 1{\cdot}47$.

(5) *Contrast between the Behaviours of Paraffins and the Corresponding Olefins in Explosions of* $C_2H_{2n+2} + \frac{n}{2}O_2$ *and* $C_nH_{2n} + \frac{n}{2}O_2$ *Mixtures.*—I now come to a most arresting and significant feature of the experimental evidence to which I would invite the closest attention. It is that, whereas all the gaseous hydrocarbons of the C_nH_{2n} series (*i.e.*, ethylene, propylene, trimethylene, and butylene) on explosion with a proportion of oxygen corresponding with $C_nH_{2n} + \frac{n}{2}O_2$ always yield substantially carbonic oxide and hydrogen without any separation of carbon or material steam formation—as though there had been a preferential burning of their carbon in accordance with the equation $C_nH_{2n} + \frac{n}{2}O_2 = nCO + H_2$—yet, on the other hand, explosions of the corresponding members of the paraffin series (*i.e.*, ethane, propane, and butane) with oxygen in the $C_nH_{2n+2} + \frac{n}{2}O_2$ proportion, all result in dense clouds of carbon, steam, methane, and oxides of carbon, just as has already been seen in the case of the $C_2H_6 + O_2$ mixture.

Experiments. Although this crucial point has already been demonstrated with $C_2H_4 + O_2$ and $C_2H_6 + O_2$ media, respectively, we will now reinforce it by two further series of explosions, namely, (*a*) of olefin $C_nH_{2n} + \frac{n}{2}O_2$ (*e.g.*, propylene and butylene) mixtures at $p_1 = 500$ mm., and (*b*) of the corresponding paraffin $C_nH_{2n+2} + \frac{n}{2}O_2$ (*e.g.*, propane and butane) mixtures at $p_1 = 730$ mm. It will be seen that, in striking contrast with the olefin explosions, where neither separation of carbon nor any material condensation of steam occurs, the corresponding paraffin explosions result in dense clouds of carbon, followed after cooling by a copious condensation of steam, and subsequent examination would also reveal both aldehyde and methane formation. In Table II are shown full details of similar experiments carried out in my laboratories.

Such results (it may be added) are entirely consistent with the hydroxylation theory, which would require separation of carbon and much steam as well as some aldehyde survival

TABLE II.

Comparative Explosions of $C_2H_{2n} + \frac{n}{2}O_2$ *and* $C_nH_{2n+2} + \frac{n}{2}O_2$ *Mixtures.*

			$C_4H_8 + 2O_2$.				
Original mixture.	$C_2H_4 + O_2$.	$C_2H_6 + 1\frac{1}{2}O_2$.	*n*-C_4H_8.	*iso*-C_4H_8.	$C_2H_6 + O_2$.	$C_3H_8 + 1\frac{1}{2}O_2$.	$C_4H_{10} + 2O_2$.
p_1, mm.	545·3	563	479	438	698	592	617
p_2, mm.	1053·5	1244	1169	982·5	1048	1028	1221
p_2/p_1	1·93	2·20	2·43	2·20	1·50	1·737	1·978
Percentage ...CO_2	0·3	0·1	0·90	1·40	4·30	4·1	3·7
comparison ...CO	50·0	50·9	50·50	50·20	34·75	38·0	41·7
of gaseous ...C_nH_m	nil	1·0	0·65	1·90	3·90	3·8	3·4
products : ...CH_4	1·7	1·5	1·60	3·00	9·20	8·0	8·5
...H_2	48·0	46·5	46·35	43·50	47·85	46·1	42·7
	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.
Units in original mixture	545 545 272	675 675 338	630 630 322	584 584 292	698 1047 349	708 945 355	823 1018 411
,, gaseous products	547 541 267	677 634 318	634 590 305	574 515 260	587 756 227	593 700 237	741 790 299
Difference	— — —	— 41 20	— 40 17	10 69 32	111 291 122	115 245 118	82 238 112
General features	Sharp bluish flames. No separation of carbon. No (or only just visible) condensation of steam. Products of *iso*-butylene explosion contained $H_2C{:}O$.				Lurid yellow-red flame, copious carbon deposit and considerable H_2O-formation. Condensates all gave aldehyde-reaction.		

in the paraffin explosion, while the corresponding olefin explosions can be brought into line with it by supposing their substantially involving successive eliminations of $H{\cdot}\dot{\underset{\cdot}{C}}{\cdot}OH \longrightarrow H_2C{:}O$ (formaldehyde) groups which, rapidly decomposing in the flame, yield (as does formaldehyde) equal volumes of carbonic oxide and hydrogen without any carbon separation or material steam formation, somewhat as follows :

$$\begin{tikzcd}
CH_3{\cdot}CH{:}CH_2 \arrow[r] & CH_3{\cdot}CH{:}CH{\cdot}OH \arrow[r] & CH_2{:}CH_2 \arrow[d] & + \underbrace{H_2C{:}O}_{CO + H_2} \\
 & & CH_2{:}CH{\cdot}OH \arrow[r] & \underbrace{\underbrace{CH(OH){:}CH{\cdot}OH}_{2H_2C{:}O}}_{2CO + 2H_2}
\end{tikzcd}$$

(6) *Explosions of Olefin–Oxygen Mixtures containing Less Oxygen than* $C_nH_{2n} + \frac{n}{2}O_2$.—Another very remarkable feature of the explosion of olefin–oxygen mixtures is that, whereas little or no steam is produced when the oxygen present corresponds with the $C_nH_{2n} + \frac{n}{2}O_2$ proportion, more and more of it will appear in the cooled products if and as the oxygen ratio is progressively diminished therefrom, even though progressively more carbon is simultaneously deposited.

Experiment. To illustrate this point, mixtures of $3C_2H_4 + 2O_2$, $C_3H_6 + 1\frac{1}{4}O_2$, and $C_4H_8 + 1\frac{1}{2}O_2$, respectively, will now be exploded in sealed bulbs at initial pressures of *ca.* 600 mm. It will be seen that in each case the flame is accompanied by a copious separation of carbon, and an inspection of the cooled products will enable the condensation of steam to be verified. Particulars of similar experiments previously carried out in my laboratories are shown in Table III.

TABLE III.

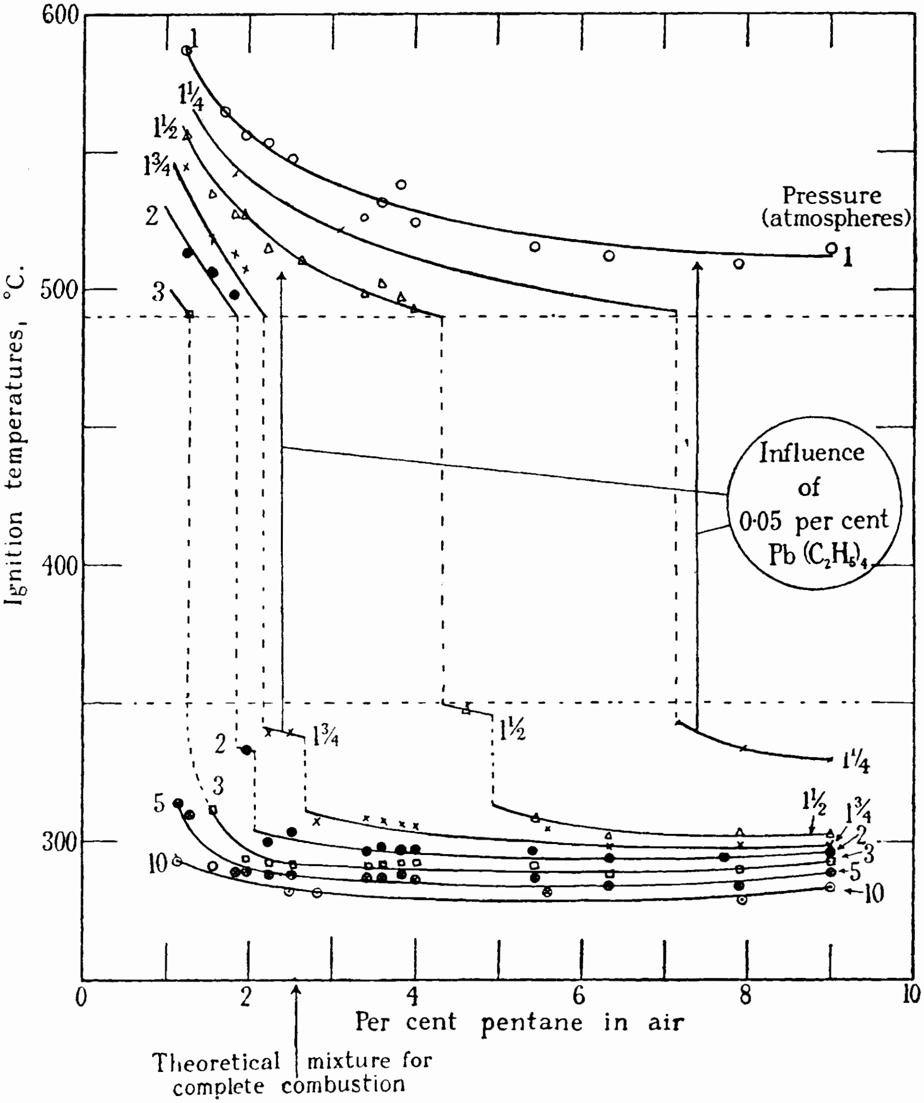
Olefin–Oxygen Explosions.

Original mixture.		$3C_2H_4 + O_2$.	$C_3H_6 + 1\frac{1}{4}O_2$.	$C_4H_8 + 1\frac{1}{2}O_2$.
p_1, mm.		562·3	682·0	574·0
p_2, mm.		816·4	1213·0	1094·0
p_2/p_1		1·45	1·78	1·90
Composition, %, of gaseous products :	CO_2	2·50	3·20	3·50
	CO	37·20	43·05	41·40
	C_nH_m	6·40	4·90	4·75
	CH_4	6·50	6·90	7·55
	H_2	47·40	41·95	42·80
		C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.
Units in original mixture		670 670 227	918 918 376	899 899 347
,, gaseous products		482 572 172	763 766 300	678 713 265
Difference		188 98 55	155 152 76	221 186 82
Percentage of original O_2 in condensed products as H_2O and aldehyde		24·4	20	23·6

Again, such results are what might be anticipated from the hydroxylation theory; because, whenever the oxygen originally present in the medium is *less* than that which is requisite for the successive elimination as $H_2C{:}O$ of *all* the postulated ${:}CH_2$ units, there must finally be some breakdown of a $\cdot CH{:}CH\cdot OH$ complex with production of both carbon and steam. Moreover, the fact that in such circumstances the proportion of the original oxygen surviving as steam in the cold products increases always with a growing oxygen-defect in the original medium strongly supports " hydroxylation."

FIG. 2.

Influence of Pressure on the Ignition Temperatures of Pentane–Air Mixtures (Townend and Mandlekar).



(7) *The Influence of Pressure upon the Spontaneous Ignition of Hydrocarbon–Air Mixtures.*—Before leaving this part of my subject, I want briefly to refer to an important discovery concerning the influence of pressure upon the spontaneous ignition of hydrocarbon–air mixtures recently made by my colleague Dr. D. T. A. Townend (Townend and Mandlekar, *Proc. Roy. Soc.*, **1933**, *A*, **141**, 484) which, besides its theoretical interest, has a direct bearing upon the problem of " knock " in petrol–air engines.

Dr. Townend's experiments have so far comprised the explosive ranges of *n*- and *iso*-butanes as well as of *n*-pentane with air and he is now extending them to those of other hydrocarbons. He has found that, as the pressure is progressively raised from 1 to 15 atmospheres in each case, what may be termed the observed ignition temperatures fall into two well-defined groups separated by a temperature range in which no ignition points occur.

This may be illustrated by the accompanying diagrams (Fig. 2) summarising his results for pentane–air mixtures in which ignition temperatures for a series of pressures between 1 and 10 atmospheres are plotted (ordinates) against percentages of pentane (abscissæ) in the media concerned. It will be seen that whereas at atmospheric pressure the observed ignition-points all lie above 490°, at all pressures above 5 atmospheres they all lie below 350°. At each intermediate pressure between 1 and 5 atmospheres transference of an ignition point from the higher to the lower group occurs sharply on the attainment of a definite critical transition pressure which varies slightly with the composition of the medium. Moreover, addition to the medium of an " anti-knock " compound, such as lead tetraethyl, at pressures near such " critical transition pressure " effects a transfer of its ignition-point from the lower to the higher group. Similar results have accrued with the other hydrocarbons examined.

In practice, whereas " knock " in a given medium would thus seem conditioned by its pressure permitting of ignition at the *lower* of the two temperature ranges, within a certain intermediate pressure-range it may be obviated by the presence of an " anti-knock." The explanation of such occurrence may possibly be connected with the influence of pressure upon the stability of some one or more of the oxygenated compounds intermedially formed during the hydrocarbon combustion.

V. CONCLUDING REMARKS: HYDROXYLATION VERSUS PEROXIDATION.

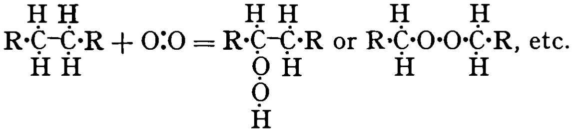
(1) *General.*—In addition to the experiments which have been specifically referred to, many others have been done embracing every possible condition between slow combustion and detonation, including pressures from as low as one-third of an atmosphere up to as high as 100 atmospheres, and the cumulative evidence of all leaves no doubt in my mind but that " hydroxylation " affords the best general view of the normal course of hydrocarbon combustion, and as such I commend it to you. It should not, however, be interpreted or applied too rigidly; for a theory should be judged by its ability to give a consistent interpretation of the facts to which it applies, and it may be accepted as a serviceable implement so long as it succeeds in doing so and until a better one is available. " Let us beware of idols."

(2) *Directness of the Oxidation.*—I feel bound to say, however, that, while agreeing with H. E. Armstrong as to the combustion involving successive hydroxylations, I differ from him as to the mechanism thereof. For while (to take the case of methane) he regards each step as involving the intervention of steam and the simultaneous formation of hydrogen peroxide, thus: $CH_4 + HO{\cdot}H + O{:}O = CH_3{\cdot}OH + H_2O_2$, etc., my own experiments lend no support to such a view. For they have shown that, while intensive drying by phosphoric oxide has little or no effect upon the slow combination of either $C_2H_4 + O_2$ or $C_2H_2 + O_2$ mixtures at *ca.* 430° and 415°, respectively, it accelerates the speeds of flame propagation through them in explosive combustion. Hence I cannot but regard the oxidation as direct, or in other words as unconditioned by the presence of steam.

(3) *The Peroxidation Theory.*—In recent years, however, there has been much talk about the initial association of the hydrocarbon and oxygen resulting in an alkyl " peroxide " rather than in a hydroxylated molecule, and in the remaining time we may profitably consider the suggestion in the light of the latest evidence available.

Alkyl peroxides (*e.g.*, $CH_3{\cdot}O{\cdot}OH$ and $CH_3{\cdot}O{\cdot}O{\cdot}CH_3$), which were first described in 1900—1 by Baeyer and Villiger (*Ber.*, 1900, **33**, 3387; 1901, **34**, 378) and have recently been re-investigated by Rieche and his collaborators (*Ber.*, 1928, **61**, 961; 1929, **62**, 218, 438), are obtained by acting upon a dialkyl sulphate with hydrogen peroxide in alkaline solution. They are unstable endothermic liquids which readily explode upon being suddenly heated or subjected to " shock," producing aldehydes and hydrogen together with hydrocarbons, alcohols, acids, and steam.

It was the late Professor Callendar (*Engineering*, 1927, **123**, 147, 182, 210) who, as the outcome of experiments upon the slow combustion of hexane—which resulted in the formation of valeraldehyde, acetaldehyde, and formaldehyde without any detectable initial hexyl alcohol, $C_6H_{13}\cdot OH$—first suggested that the initial oxidation of a hydrocarbon in air more probably involves the formation of an alkyl peroxide " *by the direct incorporation of the oxygen molecule in the hydrocarbon molecule and after collision,*" which subsequently decomposes into aldehydes and water, thus :



$$R\cdot\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdot R + O\colon O = R\cdot\underset{\underset{\underset{H}{O}}{O}}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdot R \text{ or } R\cdot\underset{H}{\overset{H}{C}}\cdot O\cdot O\cdot\underset{H}{\overset{H}{C}}\cdot R, \text{ etc.}$$

The idea was then put forward to explain " knock " in petrol engines, though it is rather difficult to see how, if valid in such connection, it can at the same time be applied to the normal course of the combustion.

Two years later, Thompson and Hinshelwood (*Proc. Roy. Soc.*, 1929, *A*, **125**, 291), after studying the kinetics of the oxidation of ethylene in silica vessels at temperatures between 400° and 500°, and finding that the rate is affected by the total pressure approximately as in a reaction of the third order, the effects depending very much more on the partial pressure of the ethylene than on that of the oxygen, suggested as a *via media* that while " *there is no doubt that Bone's interpretation of the complete course of oxidation as a process of successive hydroxylations is essentially correct . . . the first stage in the reaction is the formation of an unstable peroxide ; if this reacts with more oxygen the chain ends, but if it reacts with ethylene unstable hydroxylated molecules are formed which continue the chain.*" It should be noted, however, that they adduced no experimental proof of the actual initial formation of the assumed peroxide.

Although at first sight the notion may seem plausible enough, and obviates the difficulty which some feel of an initial termolecular reaction,* I venture to think that it is not merely unsupported by any valid experimental evidence but contrary to much that has been established.

It is not enough to show, as some have done, that during the slow oxidation of a hydrocarbon products are formed capable of liberating iodine from a solution of potassium iodide, because (at least in the presence of oxygen) aldehydes will do so. Nor would it suffice to prove the formation of some unidentified " peroxide " during the combustion process, without also proving it to be the *initial* product and not merely a peroxide incidentally formed (as we now know) during the further oxidation of an aldehyde; but so far such proof has been entirely wanting. And it seems to me that until the upholders of the peroxidation theory can produce such evidence they have no real case to go to the jury.

During the past four years, my colleagues and myself have sought diligently, but so far wholly in vain, for any such evidence in the slow combustion of methane, ethane, propane, and ethylene ; for, although we have found unmistakable signs of secondary " peroxidation " of aldehydes, there has been none of any primary peroxidation of the hydrocarbon itself. And we are of opinion that the peroxidationists have confused the two effects.

Thus, for example, in the case of ethylene—which, being unsaturated, should be prone to an initial " peroxidation," if such really does occur—we have found with its most reactive $2C_2H_4 + O_2$ mixture at 300° no trace whatever of any " peroxide," $C_2H_4O_2$, during the " induction period," although aldehyde is always discernible, and the test applied for peroxide is, if anything, more delicate than that for the aldehyde. Moreover,

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* This, however, does not seem formidable to me; for in slow combustion it may well need the combined pull of two hydrocarbon molecules to dissociate an oxygen molecule, and in flames oxygen atoms may act. Moreover, in view of the overwhelming affinity between them, it is conceivable that when a hydrocarbon molecule meets one of oxygen, the two might hold each other in transient physical association until hit by a second hydrocarbon molecule, with consequent immediate formation of two molecules of the monohydroxy-compound as the first recognisable chemical result.

during the subsequent " reaction period " no peroxide appears until there has been a fair accumulation of formaldehyde, the two reaching a maximum almost simultaneously, and the peroxide disappearing before the end of the experiment while there is still free oxygen remaining in the system. Hence it would seem that a certain accumulation of aldehyde always precedes any appearance of " peroxide," the latter (if observed at all) being dependent on the former.

These results are shown graphically in Fig. 3, where the partial pressures of each

FIG. 3.

Course of reaction in a moist $2C_2H_4 + O_2$ *medium at* 300°.

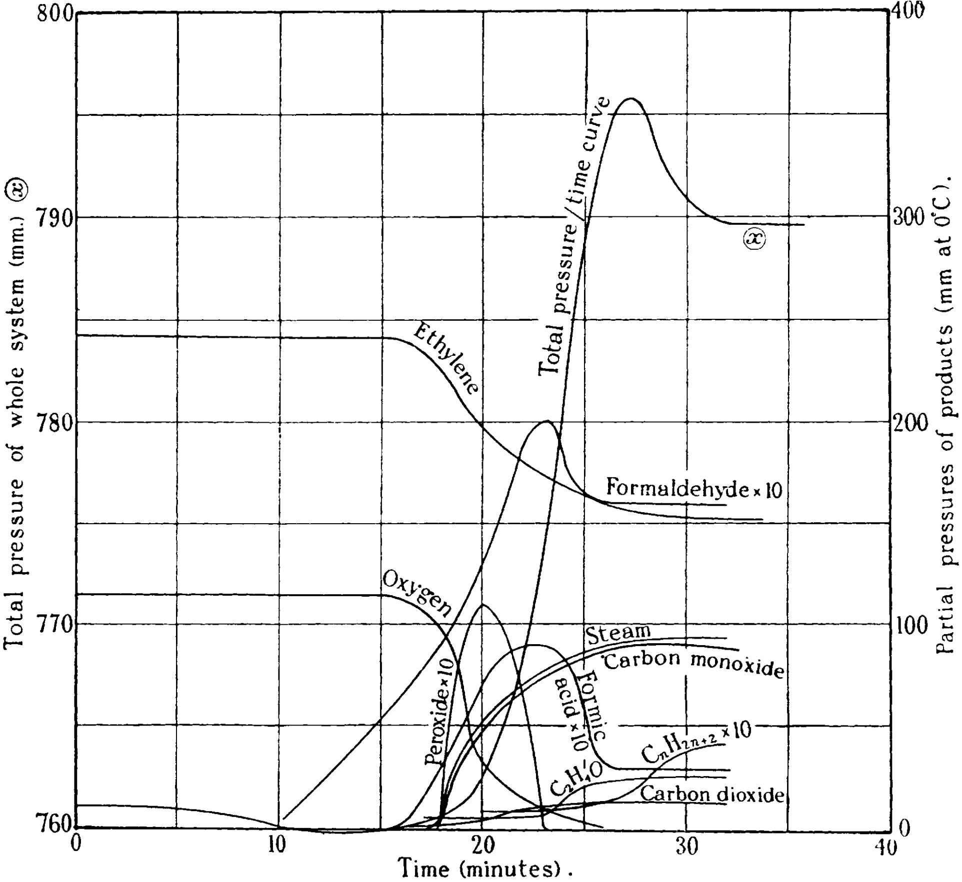


TABLE IV.

Durations of (i) *Induction and* (ii) *Reaction Periods in the Slow Combustion of Hydrocarbon Oxygen Mixtures.*

Hydrocarbon	Methane				Ethane			Propane			Ethylene			
Temperature, ° C....	447°				316°			267°			300°			
Hydrocarbon–oxygen ratio	3 : 1	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	3 : 1	2 : 1	1 : 1	1 : 2
Duration of (i) induction period (mins.)	10	3·5	10	18	3	30	60	110	170	700	25	16	44	47
(ii) reaction period (mins.)	150	35	400	*	13	35	225	14	21	32	20	16	26	330+

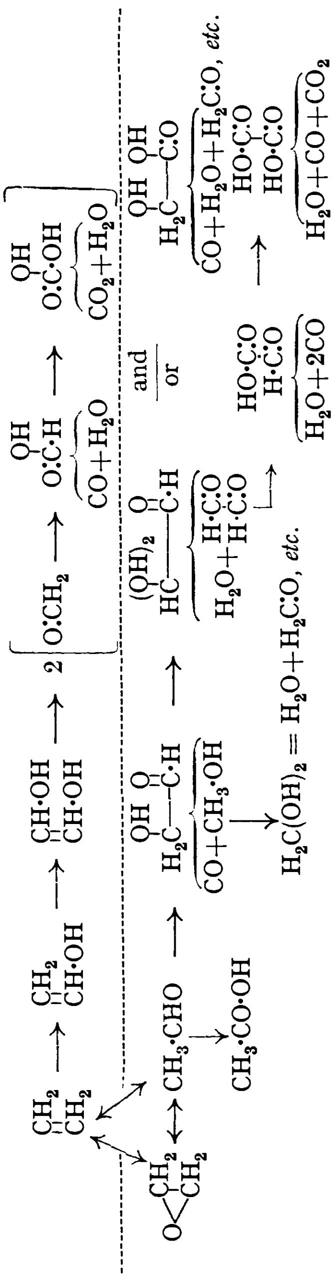
Note.—The methane–oxygen and ethylene–oxygen mixtures were all saturated with moisture at room temperature, but all the others were dried by phosphoric oxide.

* Too long to be measured.

constituent in the medium, as well as the total pressure, are plotted against time throughout the whole course of the experiment. It should be noted, however, that whereas the partial pressures of ethylene, C_2H_4O-isomerides, steam, oxygen, and oxides of carbon are plotted in millimetres as found, those of formaldehyde, formic acid, C_nH_{2n+2}, and " peroxides " have all been multiplied by 10 in order to make them more easily read.

The conclusion that such peroxide-formations are accidental rather than a normal and constant feature during such slow oxidations has been reinforced by the results of Newitt's experiments upon the pressure-oxidations of the various hydrocarbons he has studied. For while he has isolated alcohols, aldehydes, and acids in relatively large quantities, he has never been able to detect any trace of peroxide from first to last during the process. And in view of the consideration that pressure should favour the stability of any peroxide formed, his failure to find any is significant.

In order to demonstrate these points to you, the relevant experiments were carried out in my laboratories yesterday and I have here aqueous solutions of the soluble reaction products obtained. The first three are those obtained (i) towards the end of the " induction period," (ii) midway through the " reaction period," and (iii) at the end of an experiment at 300° with a $2C_2H_4 + O_2$ mixture. On applying the usual qualitative tests we shall find that whereas (i) and (iii) contain aldehyde but no peroxide, (ii) contains both. The fourth solution is from a pressure-oxidation of ethylene at 240° and 50 atms. pressure and on testing it we shall find aldehyde but no peroxide. Indeed the full scheme for the slow oxidation of ethylene, embodying our latest results, is as annexed.



Finally it may be urged against the " peroxidation theory " that (as already stated) in the slow oxidation of gaseous hydrocarbons at atmospheric pressure, the most reactive mixture is not the equimolecular but one in which the hydrocarbon : oxygen ratio is 2 : 1, *i.e.*, corresponding with the alcohol-forming proportion. This is shown in Table IV.

Against all this weighty rebutting evidence, what have we on the other side so far? I venture to think nothing more than surmise without any tangible experimental proof, for which so far we have waited in vain. My mind is still as always open to conviction upon sufficient experimental evidence forthcoming; but it must be unmistakably clear, and pertaining to such gaseous hydrocarbons as have been considered herein; because the higher one ascends in a given series of hydrocarbons, the more complex is the sequence of changes involved, and it becomes well-nigh impossible to discriminate between the main and side reactions, or between primary and secondary happenings.

Doubtless in such cases, there is more room for side reactions of all kinds, some of which may involve incidental " peroxidation," especially of aldehydes; therefore I wish it to be understood that, while on present evidence rejecting the " peroxide " theory as applied to the main and normal course, and especially to the initial stage, of hydrocarbon combustion, I by no means exclude incidental " peroxidations " of intermediate products. But even as regards " knock," nothing as yet is really proven, and it seems to me that Dr. Townend's recent discovery, to which reference has been made, suggests an alternative explanation of the phenomenon which it may be hoped he will thoroughly explore.

In conclusion I desire to express my indebtedness and thanks to my colleagues Drs. D. M. Newitt and D. T. A. Townend, as well as to Messrs. L. E. Outridge and H. F. Rance, for their devoted help in carrying out the experiments included in my Lecture.