

of August 29, 1930, when a terrific thunderstorm of blinding flashes came to St. Marybourne from Winchester, but no flashes were clear of obstruction by rain until they were close up.

Dr. Halliday has made no reference to the stereoscopic method of examination. In his photographs the process of measurement with a micrometer microscope is easy as the aberration is longitudinal. In my photograph where this is transverse, I found measurement with Mr. Loomis's fine micrometer microscope too tedious and the stereoscopic method much more convenient.

I should like in conclusion again to appeal to lightning observers suitably placed to initiate a lightning flash with a rocket. I gave some indica-

tion of what to do in my article in NATURE of November 20, 1926, but if anyone should care to consider this more closely, I would recommend the construction of a 'towering rocket' of suitable proportions which should have great persuasive power. Long ago I made a 1 lb. rocket to carry a 6 oz. rocket in its head and this again to carry a 2 oz. rocket which, of course, had the usual stars. The conducting trail which such a combination creates in a very short time and up to an immense height, should initiate a flash almost with certainty if a new flash should be becoming due.

¹ *Phil. Mag.*, Feb. 1933.

² NATURE, 118, 749, Nov. 20, 1926.

³ NATURE, 122, 310, Sept. 1, 1928; 124, 54, July 13, 1929; and 127, 425, March 14, 1931.

Researches on Gaseous Combustion*

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HYDROCARBON COMBUSTION

IN reviewing, in my recent Bakerian lecture, the principal researches upon the combustion of hydrocarbons, the importance was stressed of a balanced judgment embracing the whole range of conditions from slow combustion through flames and explosions right up to detonation. For it is only by taking all conditions into account comprehensively that a true view of the subject can be gained.

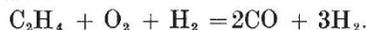
It was shown how the hydroxylation theory is capable of expressing the principal facts of both the slow and explosive combustion of gaseous hydrocarbons. For although the conditions prevailing in flames are obviously much more complex than those of slow combustion, the main course of the chemical changes concerned therein may be satisfactorily interpreted on the supposition that the result of the initial encounters between hydrocarbon and oxygen is the same in both, namely, the formation of an 'oxygenated' which (except with acetylene) is a 'hydroxylated' molecule. Undoubtedly, at the higher temperatures of flames, secondary thermal decompositions occur and play a more conspicuous rôle than in slow combustion; but there are the strongest experimental grounds for believing that they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence thereof. In particular, all the evidence is quite decisive against such views as that of a 'preferential' combustion, whether of hydrogen or carbon, or that in an explosion flame the hydrocarbon molecule is primarily resolved into its elements before being burnt.

Experiments were made showing that 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 deficient in oxygen the hydrocarbon is burnt, as it were, preferentially. Perhaps the most striking experiment of all consisted in exploding a mixture of 25 per cent of acetylene and 75 per cent of electrolytic gas in

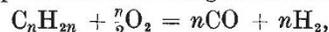
a stout glass bulb at a pressure of (say) 500 mm. (higher could be used but for the danger of shattering the vessel). A sharp bluish flame filled the vessel, but neither carbon separated nor did any steam condense on cooling, the products consisting of carbonic oxide and hydrogen with traces only of carbonic anhydride or of methane, in accordance with the equation:



A similar result was also obtained on exploding a mixture of equal volumes of ethylene, hydrogen and oxygen, thus:—



Another most arresting and significant feature of the evidence, also illustrated experimentally, was that whereas all the hydrocarbons of the C_nH_{2n} series, that is, ethylene, propylene, trimethylene and butylene, on explosion with a $\text{C}_n\text{H}_{2n} + \frac{n}{2}\text{O}_2$ proportion of oxygen always yield substantially carbonic oxide and hydrogen only, as though there had been a preferential burning of their carbon, thus:



explosions of corresponding members of the $\text{C}_n\text{H}_{2n+2}$ or paraffin series (that is, ethane, propane or butane) with oxygen in the $\text{C}_n\text{H}_{2n+2} + \frac{n}{2}\text{O}_2$ proportion, all result in dense clouds of carbon, steam, methane and oxides of carbon. This striking difference between the behaviours of corresponding paraffins and olefines accords well with the hydroxylation theory.

Moreover, in regard to olefine explosions, another significant fact is that, so soon as the proportion of oxygen in the medium is progressively reduced below the $\text{C}_n\text{H}_{2n} + \frac{n}{2}\text{O}_2$ proportion, steam (as well as carbon) begins to appear in the products and relatively increases in amount as the oxygen content diminishes. This was demonstrated by exploding a $3\text{C}_2\text{H}_4 + 2\text{O}_2$ mixture and it points unmistakably to the initial formation of 'hydroxylated' molecules in such explosions.

In recent years, however, the suggestion has been made that the initial association of hydro-

* Substance of the Bakerian Lecture (*Proc. Roy. Soc.*, A, 137, 243-274) and papers read afterwards at the Royal Society on Nov. 10, 1932 (*ibid.*, A, 137, 57-83).

carbon and oxygen molecules in explosions results in a 'peroxidation' rather than a 'hydroxylation', but on closer examination the evidence of such 'peroxidation' has broken down completely. In the first place, whereas in no case of slow combustion of the gaseous hydrocarbons referred to has the postulated initial 'peroxidation' been proved by the isolation of the particular peroxide involved, abundant evidence of the initial formation of alcohols has been forthcoming from experiments on the pressure-oxidation of methane and ethane. Secondly, in the latter case, recent experiments by Dr. D. M. Newitt and Mr. A. M. Bloch in our laboratories have afforded quantitative proof of the hydroxylation theory, no peroxides whatever being found at any stage of the process. Thirdly, in such slow oxidation, the shortest 'induction' and 'reaction' periods are obtained with 2-hydrocarbon-1-oxygen instead of with equimolecular mixtures. Fourthly, experiments upon the induction period have definitely proved that the formation of an aldehyde always *precedes* that of any peroxide, the latter being rarely (if ever) observed. Finally, the 'peroxidation' theory is countered by the results of exploding under pressure methane-oxygen mixtures of compositions intermediate between $5\text{CH}_4 + 2\text{O}_2$ and $\text{CH}_4 + \text{O}_2$. Indeed, all the evidence points to any slight peroxide formation which may sometimes be observed during hydrocarbon combustion being a relatively late and minor side occurrence dependent upon a prior formation of aldehyde.

EXPLOSIONS AT HIGH PRESSURES

In continuance of researches upon gaseous explosions at high initial pressures carried out for many years past by Drs. D. M. Newitt, D. T. A. Townend and myself at the Imperial College, we have recently published further results of experiments upon (1) hydrogen-air and carbonic oxide-air explosions at initial pressures between 250 and 1,000 atmospheres, and (2) the formation of nitric oxide in carbonic oxide-oxygen-nitrogen flames and explosions.

The previous work had resulted (*inter alia*) in the discovery of a nitrogen activation in $\text{CO-O}_2\text{-N}_2$ explosions at high initial pressures, due to an absorption by nitrogen molecules of the radiation emitted by the burning carbonic oxide, the effect steadily increasing with the density of the medium but apparently approaching a maximum at initial pressures of about 150 atmospheres, although its intensity relative to the total kinetic energy developed had been greatest at $P_1 = 75\text{--}100$ atmospheres. The new experiments were designed to show not only (a) how much further the effect would increase with the density of the medium, but also, (b) in presence of excess of oxygen, how much of the nitrogen thus activated would form nitric oxide during the explosions, the latter consideration being of importance from the point of view of a possible commercial process for the direct fixation of nitrogen.

In investigating (a), a special super-pressure bomb, with a cylindrical explosion chamber 3 in. long and $1\frac{1}{2}$ in. in diameter (capacity 115 c.c.), capable of withstanding explosion pressures up to 10,000 atmospheres (with a safety factor of 4), was employed; and the pressures actually developed far exceeded any yet recorded in any explosion experiments. For determining (b), a $2\text{CO} + 3\text{O}_2 + 2\text{N}_2$ mixture, which is the most favourable of all to the formation of nitric oxide, was exploded at various initial pressures between 40 and 88 atmospheres in a nickel-steel bomb (explosion chamber = 990 c.c.) in such-wise that at some predetermined moment during the explosion a steel disc partition was burst suddenly, liberating the gaseous products into a large 'expansion chamber' (capacity = 38 litres) from which they were afterwards withdrawn for analysis.

Theoretical hydrogen-air (that is, $2\text{H}_2 + \text{O}_2 + 3\cdot76\text{N}_2$) explosions went off quite normally up to an initial pressure (P_1) of 500 atmospheres, the 'explosion time', t_m , being of the order 0.015-0.022 sec., but tending to increase with the pressure. The subsequent rate of cooling accorded with Newton's law throughout, being uncomplicated by any appreciable exothermic effect; the amount of steam-dissociation at the maximum explosion temperature (T_m) was always less than 0.5 per cent. At $P_1 = 750$ atmospheres, however, such violent detonation was instantaneously set up that the screw threads of the bomb fittings were seriously damaged and it was deemed too dangerous to proceed to any higher pressure.

Explosions of theoretical carbon monoxide-air (that is, $2\text{CO} + \text{O}_2 + 3\cdot76\text{N}_2$) mixtures were successfully carried out at various initial pressures up to and including 1,000 atmospheres, with results showing that the nitrogen activation had reached a maximum at $P_1 = 350$ atmospheres, when its exothermic effect on the cooling curve was equivalent to some 12.5 per cent of the total kinetic energy developed. In explosions at $P_1 = 1,000$ atmospheres, $t_m = 0.24$ sec., and the maximum gauge pressure (P_m) developed was 7,100 atmospheres (about 46 tons per sq. in.), with T_m just under 3000°K . The percentage dissociation of carbon dioxide at T_m ranged from 2.4 at $P_1 = 250$ up to 5.5 with $P_1 = 1,000$ atmospheres.

The $2\text{CO} + 3\text{O}_2 + 2\text{N}_2$ explosions (b) showed not only the beneficial influence of pressure upon the nitric oxide formation, but also that in all cases it begins during the 'combustion period' and extends far into the 'cooling period'. Thus, whereas at $P_1 = 70$ atmospheres only about 3.3 per cent of nitric oxide had been formed up to the moment of maximum pressure ($T_m = 2900^\circ\text{K}$) as much as 5.4 per cent was present some 0.06 sec. thereafter; and at $P_1 = 88$ atmospheres the maximum nitric oxide formation would be of the order of 6 per cent. Such yields of nitric oxide are many times higher than any previously obtained in explosions.