

PART II. (B) HYDROCARBONS.

FREE RADICALS IN THE THERMAL DECOMPOSITIONS AND COMBUSTION OF HYDROCARBONS.

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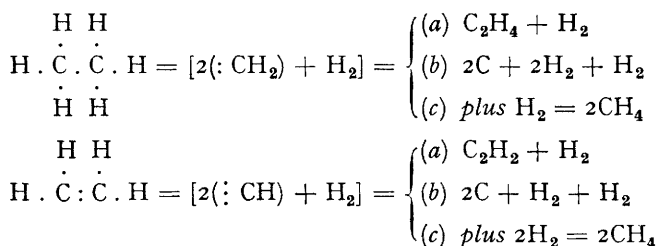
*Communicated 29th September, 1933.***Thermal Decompositions.**

The supposition that free radicals are formed in the thermal decompositions of hydrocarbons is no new thing. As long ago as 1908, in discussing the results of my experiments (in conjunction with H. F. Coward)¹ upon the thermal decompositions of methane, ethane, ethylene and acetylene, respectively, at various temperatures between 500 and 1200° C., I found it necessary to postulate the momentary formation and separate existence of such "residues" as $\cdot\text{CH}$, $\cdot\text{CH}_2$, and possibly also $\cdot\text{CH}_3$, and their subsequent hydrogenation (whenever the medium contains sufficient hydrogen) to methane.

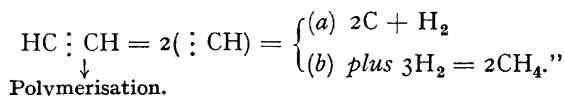
In view of the present discussion perhaps it may be of interest to quote the following two paragraphs from the paper in question (*loc. cit.*, pp. 1202-1203), in which such theory was first propounded, namely: "In the case of ethane and ethylene, it may be supposed that the *primary* effect of high temperature is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise to (in the event of dissolution) residues such as $\cdot\text{CH}_2$ and $\cdot\text{CH}$. These residues, which can only have a very fugitive separate existence, may subsequently either (a) form $\text{H}_2\text{C}:\text{CH}_2$ and $\text{HC}:\text{CH}$, as the result of encounters with other similar residues, or (b) break down directly into carbon and hydrogen, or (c) be directly "hydrogenised" to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure,

¹ *J. Chem. Soc.*, **93**, 1197-1228, 1908.

and amount of hydrogen present. The whole process may be represented by the following scheme :



and "In the case of acetylene, the main primary change may be either one of polymerisation or of dissolution, according to the temperature, and if the latter, it may be supposed that the molecule breaks down across the triple bond between the carbon atoms, giving rise to $2(\cdot \text{CH})$, and that these residues are subsequently either resolved into carbon and hydrogen or 'hydrogenised,' according to circumstances, thus :



The supposition that such "residues" primarily formed during the thermal decomposition of the hydrocarbons in question, are subsequently "hydrogenised" to methane, was not only needed to explain the large quantities of it formed during many of the experiments, but was supported by a further three series of comparative experiments on the relative amounts of methane formed when either ethane, ethylene or acetylene, respectively, each diluted to an equal degree with (a) nitrogen, and (b) hydrogen is completely decomposed at 800° under conditions precluding any sensible loss of methane. The results were as follows :—

		Percentage Methane in Final Medium.				Mean.
I. <i>Original Mixture</i>	(a) $\text{C}_2\text{H}_6 + 3\text{N}_2$	18.5,	17.15,	18.3,	18.7	18.15
	(b) $\text{C}_2\text{H}_6 + 3\text{H}_2$	42.9,	38.0,	43.9,	40.19	41.25
Ratio $\frac{41.25}{18.15} = 2.27.$						

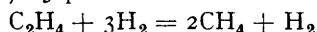
Thus in (b) 82.5 per cent. of the theoretical



was realised.

		Percentage Methane in Final Medium.				Mean.
II. <i>Original Mixture</i>	(a) $\text{C}_2\text{H}_4 + 3\text{N}_2$	15.45,	13.7,	13.4,	12.65	13.8
	(b) $\text{C}_2\text{H}_4 + 3\text{H}_2$	42.6,	40.86,	44.3,	46.35	43.5
Ratio $\frac{43.5}{13.8} = 3.15.$						

Thus in (b) 65 per cent. of the theoretical

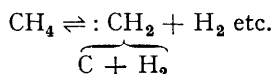


was realised.

		Percentage Methane in Final Medium.				Mean.
III. <i>Original Mixture</i>	(a) $C_2H_2 + 3N_2$	6.9,	5.05,	5.7,	5.0	5.65
	(b) $C_2H_2 + 3H_2$	26.75,	25.0,	30.4,	27.3	27.35

$$\text{Ratio } \frac{27.35}{5.65} = 4.84.$$

In the case of methane, although I then concluded that, within the temperature range referred to, "it decomposed for the main part *directly* into carbon and hydrogen, and the process, which is probably reversible at all temperatures, is . . . chiefly a surface phenomenon," in the light of subsequent researches I should now regard the main primary decomposition as probably involving the formation of $:CH_2$ radical, thus:—



and although some $:CH$ and $.CH_3$ may possibly also be produced simultaneously, the relatively insignificant (and often inappreciable) proportion of acetylene produced in my experiments make me at least doubtful about $:CH$ being formed. In this regard I think the experiments described in the paper (p.) contributed to the discussion by L. Belchetz are significant, and in general I agree with his conclusions.

Combustion.

Although doubtless there is spectrographic evidence of the presence of free radicals such as $.CH_3$, $:CH_2$, $:CH$, as well as of $C:C$, in the inner cone of hydrocarbon flames, where the oxygen supply is very restricted, the question of how they arise, and what part they may subsequently play, is one of great complexity, and it behoves us to be extremely cautious about erecting hypotheses on insufficient foundation. For it is ground, full of pitfalls for the unwary, on which even "angels may fear to tread."

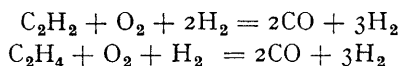
My own researches on hydrocarbon combustion during the past 40 years or more lend no support for any *primary* formation of such radicals. As already set forth in my recent Bakerian Lecture on the subject,² slow combustion oxidation proceeds by successive stages of "hydroxylation" the *primary* products being undoubtedly *methyl alcohol*, in the case of methane, *ethyl alcohol* in that of ethane, *vinyl alcohol* in that of ethylene, to confine ourselves to the simpler hydrocarbons. Although cumulative evidence on this point is now overwhelmingly strong, it cannot be adequately set forth in the space at my disposal in this paper; but it is fully dealt with in numerous papers published from my laboratories during 1902-15 and 1925-33, but particularly in those during the latter period; it is also summarised in my Bakerian Lecture² and will be further elaborated in an experimental lecture which I have undertaken to give next month to the Chemical Society in London. I doubt whether "free radicals" play much (if any) part in such slow combustion as we have studied at temperatures below (say) 300° and 450° and pressures varying between 0.5 and 100 atmospheres.

In regard to explosive combustion, although the conditions prevailing in hydrocarbon flames and explosions are obviously more com-

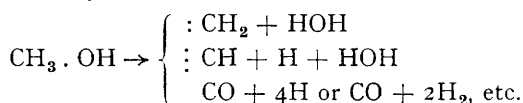
² *Proc. Roy. Soc.*, **137A**, 243-274, 1932.

plex than those of slow combustion, the experimental evidence convinces me that the result of the initial encounter between hydrocarbon and oxygen is the same in both, namely, the formation of an "oxygenated" (and usually an "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; but there are the strongest reasons for believing that they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence thereof.

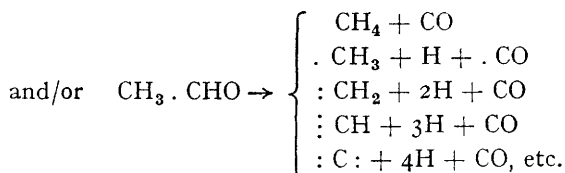
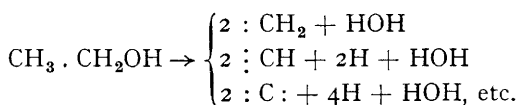
In this connection it should always be borne in mind that the affinity of a hydrocarbon greatly exceeds that of either hydrogen or carbonic oxide for oxygen in flames. Thus, on exploding a mixture of $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$ in a bomb (pressure is needed) about 95 to 97 per cent. (according to the shape and dimensions of the vessel) of the oxygen reacts with the methane. Moreover, on exploding mixtures of $\text{C}_2\text{H}_4 + \text{O}_2 + \text{H}_2$ or $\text{C}_2\text{H}_2 + \text{O}_2 + 2\text{H}_2$ at atmospheric pressure, the whole of the oxygen reacts with the hydrocarbon leaving the hydrogen untouched, thus:—



The same thing substantially applies to similar mixtures containing carbonic oxide instead of hydrogen. So great indeed is the affinity between hydrocarbon and oxygen in flames that it can scarcely be supposed that, in regions where sufficient free oxygen is present, any thermal decomposition of a hydrocarbon molecule precedes its oxidation. Hence the presence of any free radicals in hydrocarbon flames, as derived from spectrographic evidence, is much more probably due to subsequent thermal decomposition of oxygenated molecules, such as alcohols, aldehydes, etc. Thus, for example, in the inner cone of a methane flame we might conceivably have:—



and in that of an ethane flame:—



In interpreting spectrographic observations upon flames, it behoves us to proceed with due caution and sense of proportion, because (i) such evidence, however, definite it may be, is only qualitative, and (ii) as Professor Mecke says (p. 203) so far no spectrum of a free radical with more than two atoms has yet been definitely established. Hence, while spectrographic evidence may afford grounds for qualitative deductions. In particular cases, quantitative judgments are scarcely justified. In

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other words, spectrographic evidence does not enable us to distinguish between the main course of events, including primary changes, and mere side-reactions or secondary effects in flames. Therefore, while spectrography may be a potent adjunct to the chemical investigation of combustion, whether slow or explosive, it can scarcely either supersede, or even take the precedence of, purely chemical methods.
