

## Letters to the Editor.

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## Formation of Methyl Alcohol by the Direct Oxidation of Methane.

THE isolation and identification of the primary oxidation product of a hydrocarbon is so crucially important from the point of view of the theory of hydrocarbon combustion that no effort has been spared to overcome the experimental difficulties involved. For, although there is considerable agreement that the main course of the oxidation proceeds in accordance with the hydroxylation theory, during recent years there has been some controversy as to whether the initial product is an hydroxylated molecule or a peroxide.

Hitherto the cumulative weight of evidence, both direct and indirect, has been much more in favour of the initial formation of an hydroxylated molecule rather than that of a peroxide. Thus the initial formation of ethyl alcohol by the interaction of ethane and ozonised oxygen at 100° C., the results of recent studies of the slow oxidation of ethane, the formation of acetaldehyde (by intramolecular change from vinyl alcohol) during the initial stages of the slow combustion of ethylene, and what is known concerning the explosive combustion of methane at high initial pressures, have all pointed unmistakably in that direction. Nevertheless, until recently, all efforts to isolate the corresponding alcohol from the initial products of the slow interaction of one of the simpler paraffins with oxygen have been frustrated, apparently because under ordinary conditions the further oxidation of such an alcohol to the di-hydroxy stage occurs so rapidly. Hence upholders of the hydroxylation theory have always postulated an initial 'non-stop run' through the mono-hydroxy to the di-hydroxy stage.

Since the publication, in November last, of the results of a reinvestigation by Mr. S. G. Hill and myself of the slow combustion of ethane (*Proc. Roy. Soc., A*, 129, p. 434), which showed that the initial product was not a peroxide but either ethyl alcohol or some less oxygenated body, Dr. D. M. Newitt and Mr. A. E. Haffner have succeeded in obtaining substantial quantities of methyl alcohol by the direct interaction of oxygen and methane at temperatures of 360° and pressures of about 100 atmospheres. Under such conditions, and using a mixture initially containing methane and oxygen in the ratio 9 : 1, interaction was complete in a few minutes; about 17 per cent of the methane burnt was recovered from the products as methyl alcohol, another 0.6 per cent as formaldehyde, and the remainder as oxides of carbon and steam. No hydrogen was liberated, and not even a trace of peroxide formed. The methyl alcohol formed was isolated and identified by converting it into both methyl salicylate ('oil of wintergreen') and methyl *p*-nitro-benzoate (m.p. 95°), and it was estimated as methyl nitrite. A full account of these very important experiments will be published in due course by Dr. Newitt and Mr. Haffner, who are to be congratulated on having thus shown conclusively that the slow oxidation of methane proceeds throughout in accordance with the hydroxylation theory.

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## Fine Structure in the Hydrogen Band Lines.

WE have recently had an opportunity of examining the spectrum of  $H_2$  in a large Hilger quartz spectrograph crossed by a reflection echelon. The method, of which an account by one of us (W. E. W.) is being prepared for publication elsewhere, gives a record of the structure of all the lines of fair intensity. So far we have only had time to examine a small number of typical lines, but the results are very interesting. The alternate strong lines of two typical bands which end on the  $2p\ ^3\Pi_{ab}$  levels are all found to be double with the weaker component on the long wave-length side. (No description of the bands ending on the  $2p\ ^3\Pi$  levels has yet been published, but an account of these band systems by Richardson and Davidson has been communicated to the Royal Society.) For example, in the  $0 \rightarrow 0$  band of  $3d\ ^3\Sigma \rightarrow 2p\ ^3\Pi$  we find that the  $Q1$  line 5931.368 is definitely double, the components having an intensity ratio of about 3 to 1 and a separation  $\Delta\nu$  about 0.21 wave number.  $Q3 = 6002.816$  is an incompletely resolved doublet with  $\Delta\nu$  about 0.17.  $R2 = 5938.620$  is an unresolved doublet with  $\Delta\nu$  about 0.11.  $R4 = 5982.561$  is not a simple line, but it is too weak and hazy to estimate the separation. In the  $1 \rightarrow 1$  band of the same system  $Q1 = 6021.273$  is a very clear doublet with intensity ratio about 5 to 3 and  $\Delta\nu$  about 0.21.  $R2 = 6027.977$  is an unresolved doublet with  $\Delta\nu$  about 0.08.

We can compare the foregoing with typical lines of the  $0 \rightarrow 0$  band of the  $a$  system  $3p\ ^3\Pi_{ab} \rightarrow 2s\ ^3\Sigma$ .  $Q1$  and  $R0$  appear to have a very close satellite on the short wave-length side of the main line.  $Q2, Q3, R2, R3$  are fairly sharp lines, but not so sharp as some lines in the spectrum.  $R1$  is a doublet with the weaker component on the short wave-length side, intensity ratio about 3 to 10, and  $\Delta\nu$  about 0.22. Unless this  $R1$  is a blend with an unclassified line, these results mean that  $3p\ ^3\Pi_b$  is complex with the stronger level lower (as in  $2p\ ^3\Pi_{ab}$ ) and so is  $2s\ ^3\Sigma$  but with the weaker level lower. The comparative magnitudes of the triplets (which we have only resolved into doublets) run  $2p\ ^3\Pi_{ab} > 3p\ ^3\Pi_b \approx 2s\ ^3\Sigma > 3p\ ^3\Pi_a$ . If  $R1$  is a blend, the width of  $2p\ ^3\Pi$  is much greater than that of the other levels, but the remaining conclusions would require reconsideration.

On the other hand, typical lines of the singlet systems such as  $4856.553 (= 0 \rightarrow 1 P5$  of  $3d\ ^1\Pi_a \rightarrow 2p\ ^1\Sigma)$ ,  $4873.010 (= 0 \rightarrow 1 Q3$  of  $3d\ ^1\Pi_b \rightarrow 2p\ ^1\Sigma)$ , and  $4822.943 (= 2 \rightarrow 4 R3$  of  $3d\ ^1\Sigma \rightarrow 2p\ ^1\Sigma)$  are sharp lines with no evidence of structure beyond temperature breadth and are definitely sharper than any of the lines so far considered. This is not due to some accidental circumstance connected with the different region of the spectrum in which they lie. For example,  $4849.303$ , which is  $0 \rightarrow 0 R1$  of  $4$  (or  $3$ )  $p\ ^3\Sigma \rightarrow 2s\ ^3\Sigma$ , and lies near these lines, is complex and asymmetric with the bulk of the energy not in the centre.  $4838.242$ , which is  $R3$  of the same band, is similar to the  $R1$  line except that it is weaker.

The measurements given above are of a preliminary character. We have a plate which looks better than the one on which they were made and we hope to improve on them. The limit of our resolution is set by the natural temperature width of the lines; it is nowhere near the limit of the instruments employed. We cooled our discharge tube in liquid air. No doubt better results could be got with liquid hydrogen, but this is not available.

These observations firmly establish the correlation between the spectrum of molecular hydrogen and that of atomic helium.

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King's College, Strand, W.C.2, Mar. 12.

<sup>1</sup> Richardson and Das, *Proc. Roy. Soc., A*, vol. 122, p. 688; 1929.