

Before the War, one of us with various collaborators had shown that, in the case of ethane: (1) primary thermal decomposition of the hydrocarbon results in hydrogen and ethylene only; this process is inhibited by the addition of nitric oxide to the ethane; (2) the formation of methane, and under certain conditions of methane and polymer together, is secondary to the formation of hydrogen and ethylene. The formation of methane, or of methane and polymer together, which is a measure of the rate of disappearance of C_2 -hydrocarbon, is the result of a single time-determining process, the rate of which is not diminished but slightly accelerated by the presence of nitric oxide.

The behaviour of ethane might be supposed to be unique, and we assume that for this reason this work has not been referred to in the papers we have mentioned. We have now proved, however, that the thermal decomposition of propane follows exactly the same course. This fact, and others of which we give details in a paper which has been communicated to the Royal Society, appear to us to justify the claim that the manner in which normal paraffin hydrocarbons decompose when heated is that which we have described. The locus of the rupture of the carbon chain is that of the ethylene bond in the product of the primary olefine. In the case of ethane and propane there can, of course, be only one olefine. In the case of butane one would expect that the primary olefine would be 1-butylene, from which the secondary products would be methane, possibly with some polymer, and propylene. But in the region of our experiments a shift in the position of the double bond would give rise, in the first instance to some dimethyl-ethylene, the secondary products from which would be ethane and ethylene. This is what is actually observed.

We believe that the results which we have obtained places our knowledge of this very important set of reactions on a firm experimental foundation.

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It is not correct to say that the work from this laboratory referred to is based upon the 'assumptions' (1), (2) and (3) of the communication from Mr. C. G. Silcocks and Prof. M. W. Travers. That the reactions are partly chain reactions, and that in many cases pressure change is quantitatively proportional to decrease in amount of original paraffin, represent considered conclusions from detailed experiment. (1) has never been stated: the formation of methane and olefine has been given as one of several simultaneous modes of decomposition of the higher paraffins.

The writers appear to think that the primary and predominant formation of ethylene and hydrogen from ethane is incompatible with a chain reaction involving alkyl radicals. Reference to almost any text-book on chemical kinetics shows that this would be an error. (According to a generally accepted scheme—not devised by us—the ethylene is formed by breakdown of ethyl radicals.)

The implication of (3), that work in this laboratory has uncritically used change of pressure as a measure of reaction-rate, is wholly unfounded. Detailed analyses at different stages of various reactions of paraffins have been made repeatedly, and indirect

tests that the kinetic conclusions are independent of possible errors from this source have also been applied. One of the latest published sets of analyses is in *Proc. Roy. Soc., A*, 214, 20 (1952), and here it is again specifically shown that change of pressure gives a good measure of initial rate. The results also contradict decisively Prof. Travers's contention that the higher paraffins would give primarily olefine and hydrogen only. With normal butane at 530° C. and 1,400 mm. initial pressure, when the increase of pressure is 145 mm. the percentages of hydrogen, butene, methane and ethane in the products are, respectively, 2.14, 4.1, 31.4 and 13.4; when the increase of pressure is 357 mm. these percentages are, respectively, 2.14, 3.9, 32.9 and 14.5 (the analyses are by mass spectrometer). The other constituents are also consistent with primary formation of lower paraffin and olefine.

Ethane itself could not, of course, give methane and olefine in one step; that it gives methane by some process is already known. Propane does the same; but this cannot have much bearing on the primary behaviour of higher hydrocarbons, nor upon the question whether and to what extent the reactions involve chain processes. Steacie and Puddington¹ have shown that the primary decomposition of propane gives approximately equal amounts on one hand of propylene and hydrogen and on the other of methane and ethylene.

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¹ *Canad. J. Res., B*, 16, 411 (1938).

Autoradiography of Metal Surfaces using a Radiochemical Method

A NUMBER of methods have been suggested for the autoradiographic study of metal surfaces. Variations of surface composition have been detected using differences in nuclear reactions occurring during irradiation¹, differences in radioactivity produced as a result of irradiation^{2,3}, and differences in contact potential leading to differences in adsorption of charged radioactive material⁴. The method described in this communication uses the different chemical reactivities of the various metal components towards some radioactive substance that forms a localized radioactive reaction product on the metal surface.

Experiments were carried out with amyl iodide containing some of the iodine-131 isotope, which has a half-life of eight days and emits both β - and γ -rays. The liquid as obtained had a specific activity of 1.5 mC./gm. It had an amber colour and probably contained free iodine, and it seems likely that this iodine, rather than the amyl iodide itself, was responsible for the chemical reactions observed.

When the liquid was placed on a clean copper surface, allowed to remain for fifteen seconds and wiped off with filter paper, a considerable amount of radioactivity remained on the copper surface. Autoradiographs of the copper surface were taken and measurements showed that the equivalent of 150 atomic layers of iodine was present on the copper surface, almost certainly in a chemically combined form. On a mild steel surface under the same conditions, the amount of activity was much less, equivalent to ten atomic layers only. Washing with cold