omission of the history since 1885. Four decades have passed, and two decades since the first publication of the work. It would appear that the progress in the science up to at least 1900 might have been given with sufficient perspective and with justice to the few surviving men. They would not be injured by a little praise while living. Such later account would be helpful especially to younger workers in the field.

H. L. F.

SPECIAL ARTICLES

THE CHEMICAL EFFECTS IN IONIZED ORGANIC GASES

ABOUT a year ago[1] we gave a preliminary account of the effect of ionizing pure ethane by means of radon (radium emanation) mixed with it. This work has since been extended, and a further preliminary report will now be made. The gases hitherto studied are methane, ethane, propane, butane, ethylene, acetylene, cyanogen, hydrogen cyanide and ammonia; other reactions studied are: oxidation of all the foregoing except ethylene and hydrogen cyanide; the hydrogenation of acetylene, ethlene and cyanogen, and the polymerization (also in the presence of nitrogen) of acetylene, of cyanogen and of hydrogen cyanide.

In methane, propane and butane the same kind of behavior was encountered as for pure ethane. The idea has been abandoned (also for ethane) that free carbon results from these reactions. In fact, it is more exact to use the term condensation (with elimination of hydrogen) instead of decomposition. The yellow or brownish color of the liquid or solid condensates we now attribute to some unsaturation, not to free carbon.

In the case of methane the pressure change at room temperature is not a safe criterion of reaction, for the pressure remains almost constant, even when analysis shows that the greater part of the gaseous product is free hydrogen which is accounted for by reaction without volume change, such as:

$$2CH_4 = H_2 + C_2H_6.$$

The condensation of a liquid from methane is much delayed, perhaps, because it must build up in successive steps from the lowest member, methane. In propane and in butane liquid appears in droplets much sooner even than in ethane, and later may pass partly into the solid state, if a sufficient quantity of radiation be absorbed by the liquid. The phenomena in propane contained in a small volume where the density of radiation at the wall was high were particularly striking; minute gelatin-like masses with sharply defined contours built up to an appreciable depth on the wall and later curled away from it; while in a larger volume with a lower radiation density only liquid appeared. In radiating methane the total pressure at 25° C. remained practically constant during the entire reaction.

In the earlier paper it was suggested that the liquid phase formed from ethane might be octane. We now know that the ratio of hydrogen to carbon in the liquid condensates is about 1.8 to 1, which would indicate some degree of unsaturation or ring compounds, or both. Analysis further shows that methane as well as hydrogen is a product of the condensation of ethane, of propane and of butane; the ratio of hydrogen to methane liberated remained constant throughout the reactions and had the following values: for ethane about 6 hydrogen to 1 methane, for propane about 4 to 1, for butane about 6 to 1. Small proportions of other saturated hydrocarbons are also found, *e.g.*, propane and butane in the ratio of 1 to 2 from ethane; and ethane and butane in the ratio of 4 to 5 from propane. Evidently, if either one hydrogen or one methane molecule can be eliminated from a di-polymer of ethane (as assumed in our former paper) the residues would be butane and propane, respectively, and so forth for other similar possibilities. If two hydrogen molecules be eliminated from the di-polymer of a saturate, unsaturation would result, as illustrated by the ratio found, 1 carbon to 1.8 hydrogen (approximately the same in the liquids from ethane, propane and butane). Probably the two reactions involving the elimination of one or of two hydrogen molecules proceed simultaneously. Evidently, by this means, starting with any saturated hydro-carbon we can get both lower and higher members until soon all the members up to quite high polymers will be represented in the mixture, thus suggesting the mixtures occurring in petroleum.

In these ionic condensations of saturated hydrocarbons the average number of molecules of hydrocarbon condensing per positive hydrocarbon ion, M/N, varies from 1.4 to 2. For the unsaturated hydrocarbons M/N is higher, for ethylene (double bond) about 5, for triple bond compounds yet higher—cyanogen, 7; hydrogen cyanide, 10; acetylene, 20,[2] the highest yet found. This shows that the ionic

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[1] SCIENCE, 60, 364, October, 1924.

[2] Professor W. Mund, of the University of Louvain, kindly communicated this value for acetylene (which we have confirmed) in advance of a forthcoming publication (*Bull.* Soc. Chem. Belg., 34, 241, May, 1925), the appearance of which has been delayed by a printers' strike in Belgium. We have also confirmed in general the results reported by Mund and Koch (*ibid.*, 34, 119, February, 1925) on the radiation of ethane, ethylene and acetylene.

clusters are larger for the double and triple bond compounds than for the saturated ones.

Cyanogen yielded a brownish to black solid resembling paracyanogen; a little nitrogen (about 5 per cent.) was liberated during the polymerization. Hydrogen cyanide gave a reddish to brown solid, which by analogy may be called "parahydrocyanic acid," while liberating about 5 per cent of permanent gas (which a preliminary analysis showed to be nitrogen). Ethylene yielded a liquid and quite a large volume of free hydrogen, as reported by Mund and Koch (*loc. cit.*) with possibly some methane. Acetylene yielded with small evolution of hydrogen (about 2 per cent. of the initial volume of acetylene) a yellow (white in the earliest stages) solid powder similar to "cuprene"[3] —also in agreement with Mund and Koch.

The oxidation of methane and of ethane proceeds completely to carbon dioxide and water at a rate satisfying the general kinetic equation previously developed for hydrogen oxidation, which is also applicable to carbon monoxide oxidation, and to many other reactions. The principle of the *exclusivity of oxidation* exhibited in the oxidation of carbon monoxide by oxygen (*J. A. C. S.*, Nov., 1925) applies strikingly to both methane and ethane; *e.g.* methane in the presence of oxygen does not liberate hydrogen as it does alone, and ethane neither liberates hydrogen, nor does liquid phase appear, except water which is easily distinguished (by appearance and freezing point) from the oily liquid droplets due to its condensation to form liquid hydrocarbons. The value for methane oxidation of $\frac{M(CH_4+O_2)}{N(CH_4+O_2)}$ is 4.4, but in the presence of 1 molar per cent. of $Se(C_2H_5)_2$ attained a value of 5.7, only slightly below the value 6, obtained for carbon monoxide. The value for ethane $\frac{M(C_2H_6+O_2)}{N(C_2H_6+O_2)}=7$, is also somewhat lower than the theoretical 9.0. The oxidation of propane is not complete to carbon dioxide and water in the earlier stages of the reaction; less oxygen disappears than required; oily droplets appear indicating partial oxidation products. This becomes yet more pronounced for butane oxidation; much less oxygen disappears per butane molecule than would correspond to complete oxidation; water and oily droplets appear and the carbon dioxide formation represents but a small part of the carbon leaving the gas phase.

The other cases of oxidation which have been studied include that of cyanogen and of acetylene. In both cases exclusively of oxidation is most striking. Acetylene gives a clear colorless liquid and none of the yellow powder (as it does alone); it combines with oxygen in a 1 to 1 ratio; little or no carbon dioxide is formed (except by secondary action upon the product on the wall). The oxidation product is one of direct addition (a polymer of CHO) which we have not identified. The ratio $\frac{M(C_2H_2+O_2)}{N(C_2H_2+O_2)}$ is not less than 16 and may be as high as 20, the value for acetylene alone. The oxidation of cyanogen gives exclusively a white powder (instead of the black polymer obtained from pure cyanogen) which is an addition product of the formula $(CNO)_x$, not described in the literature. Its properties have not yet been studied. The ratio $\frac{M(C_2N_2+O_2)}{N(C_2N_2+O_2)}$ is approximately 7, the same as for the polymerization of cyanogen, but some gaseous nitrogen and carbon dioxide are formed as the result of a split reaction. Recently we have effected the hydrogenation of acetylene and of cyanogen. The reactions are not exclusive, thus showing a marked difference from the case of oxidation, by which is meant that besides that part of the reaction which resulted in the addition of hydrogen to the unsaturated compounds, polymerization of the latter also occurred in a parallel reaction. This result had been anticipated from the general theory of the exclusivity of oxidation.

The addition of nitrogen to acetylene was attempted in a 1 to 1 mixture. No combination with nitrogen was effected. The only reaction was that of the polymerization of acetylene to give the same yellow product obtained from acetylene alone. However, it was found that although nitrogen does not react itself, its presence much enhances the rate of acetylene polymerization; the relative rate continuing to increase owing to the increasing ratio of N_2/C_2H_2 as the reaction proceeds. This is a new kind of catalysis which may be called *ionic catalysis*. It is the more striking since it was not observed in the previous cases studied. The presence of a gas which itself did not permanently enter into reaction, we had hitherto found to have no influence on the rate of reaction. For example, the accumulation of carbon dioxide does not accelerate the rate of oxidation of carbon monoxide, nor of methane, etc.; nor does nitrogen enhance the rate of decomposition of ammonia. The function of nitrogen in catalyzing the polymerization of acetylene is to furnish additional clustering and polymerizing centers in the form of N_2^+ ions. We have just found that the number of acetylene molecules condensing for each N_2^+ ion is approximately 20, the same as for each $C_2H_2^+$, and that polymerization by both routes proceeds simultaneously. In other words

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[3] Sabatier and Sanderens, Comp. rend., 130, 250 (1900); H. Alexander, *Ber. deut. Chem. Ges.*, 32, 2381 (1899).

$\frac{-M(C_2H_2)}{N(C_2H_2+N_2)} = 20$. We have also found N_2^+ ions to have a like influence in the polymerization of cyanogen and of hydrogen cyanide where again the values $\frac{M(C_2N_2)}{M(C_2N_2+N_2)} = 7$ and $\frac{M(HCN)}{N(HCN+N_2)} = 10$ are practically identified with those reported above for cyanogen and hydrogen cyanide alone. This new type of catalysis in the gas phase will be more fully considered in a subsequent paper.

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MORPHOLOGICAL CHANGES IN BACTERIUM TUMEFACIENS

In determining the location of the organism, Bacterium tumefaciens, in the crown gall disease, it has seemed desirable to study daily fixations of tissues inoculated, together with smears of the bacteria from similar cultures used for the inoculation. These studies were made daily for a period of seventy-two days for twelve subcultures.

While I am not ready to report my observations on the tissues studied nor to give in detail my study of the smears examined, I believed there is one point of sufficient interest to students of bacteria, pathogenic to plants and animals to warrant this preliminary statement.

A smear of a bean agar culture of Bacterium tumefaciens three months old carefully prepared and stained with Loeffler's methylene blue shows an amorphous mass of jelly-like substance with occasional deeply stained minute spherical bodies. On transferring a needle full of this material to a fresh bean agar media a pearly white growth appears two days later about the streak or point of inoculation. A smear of this young culture shows long rods which not infrequently present a beaded appearance. These bacilli are apparently in the stage Henrici[1] refers to as "embryonic."

The culture grows very rapidly and under favorable conditions covers an area of one and one half cm in diameter in three to five days. Bacteria from the old and young cultures tested separately on young geranium plants were found to produce the crown gall disease equally well.[2]

Daily smears made with care to avoid contamination show that the rods break up and become smaller and smaller as the age of the culture increases until after twenty days or less when the rods are replaced by small faintly staining cocci with occasional slender bacilli or filaments. The zoogleal mass generally present appears to increase with the increasing age of the culture. The cocci also seem to disappear and the entire field resembles the picture first described. Studies of transfers have been made a great number of times with the same results.

In a large number of my subcultures which were studied separately an abundance of small lenticular bodies appear which are about equal in length but a little wider than the Bacterium tumefaciens rod. Both ends of this body stain deeply with a large variety of stains. The center portion of the body is hyaline and fails to color. These bodies are undoubtedly spores. When transferred to fresh media they germinate and give rise to a rod-like body not unlike Bacterium tumefaciens in size. In old cultures these spores appear to lose their ability to stain, but may be recognized as the body most abundant in the smear. I have tried to use these spores as a guide in locating the rods of Bacterium tumefaciens in the host. Unfortunately they also appear to be lost in old overgrowths. While I am not prepared to state definitely at this time that these spores form another phase in the life of Bacterium tumefaciens, they do not interfere with the development of the crown gall disease. Smith[3] states definitely that no spores are formed by Bacterium tumefaciens.

These observations may, in a measure, explain the difficulty associated with locating the causative organism in old crown gall tissue. It appears that Löhnis's[4] studies on the life cycle of bacteria find support in my observations of Bacterium tumefaciens. It is quite possible that the various sizes ascribed to Bacterium tumefaciens by Smith, Robinson and Walkden,[5] and Riker,[6] may be due to the fact that the age of the culture studied by these authors was not taken into consideration. The cultures of bacteria I have been studying principally are Smith's hop strain of Bacterium tumefaciens.

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[1] Henrici, A. T., Science, N. S. 61, No. 1591, 644–647, 1925.

[2] Levine, Michael, *Bull. Torrey Bot. Club*, 50: 231–243, 1923.

[3] Smith, E. F., Brown, A. N., and L. McCullock, U. S. Dept. Agr. Bur. Pl. Ind. Bull. 255, 160, pls. 109, 1912.

[4] Löhnis, F., Mem. Nat. Acad. Science, 16, 1921.

[5] Robinson, W., and Walkden, H., *Ann. Bot.*, 37, 299–324, pls. 5–6, 1923.

[6] Riker, A. J., *Jour. Agr. Res.*, 25, 119–132, pls. 1–5, 1923.