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SOME CHEMICAL ASPECTS OF THE ORIGIN OF PETROLEUM[1]

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THE continuing abundance of the natural supply of liquid hydrocarbons in the form of petroleum is the modern version of the "widow's cruse" magnified to a twentieth-century scale. Little less miraculous than its abundance is the remarkable chemical complexity of the liquid mixture found in nature. No one knows the total list of hydrocarbons that compose petroleum. An old and, as it now appears, unjust charge against the petroleum industry was that it did not make sufficient efforts to learn the complete catalogue of the constituents of petroleum, multiple and variable though they were known to be.

For the past several years the American Petroleum Institute has concerned itself with the identification of the chemical constituents of certain commercial fractions of petroleum. The work has been ably conducted by Dr. E. W. Washburn, of the Bureau of Standards, and his associates. The researches which are still in progress continue to add to the evidence of the astounding complexity of even a single commercial fraction of petroleum. Several hundred fractions were obtained before the identification of a single chemical individual became possible. One of their recent achievements[2] is the proof that further fractionation is still proceeding when difference of boiling point becomes so slight (less than 0.01° C.) that it fails as a guide, while difference in index of refraction still detects progressing fractionation.

The synthesis of liquid hydrocarbons from a single gaseous member by certain methods which will be discussed later has also produced very complex mixtures. This was to be expected from the theory of the mechanism developed before the actual complexity

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[1] Address of the vice-president and retiring chairman of Section C—Chemistry, American Association for the Advancement of Science, Cleveland, December 30, 1930.

[2] *Bull.* Amer. Petroleum Inst., Vol. XI, No. 53, p. 7, Sept. 12, 1930.

was demonstrated. The methods also suggested for the first time direct means of building up heavier hydrocarbon molecules from lighter ones, in contrast with the generally known process of breaking down heavy to light ones by thermal means, as illustrated by cracking.

The great chemical complexity of the liquid hydrocarbons existing in nature raises certain very interesting chemical questions as to the origin of this degree of complexity without involving directly the problem of ultimate origin. The solution offered, or the new evidence in favor of it, may, however, throw some indirect light on the larger problem. But it is really the origin of the complexity rather than the initial source of natural hydrocarbons toward which the present discussion is directed.

Evidently, one must admit either a definite chemical reactivity among hydrocarbons enabling them to spread out from a certain center consisting of one or a small number of members in both directions, higher and lower, to give the observed complexity, or else we must admit the complexity as existent from the primary origin itself.

On *a priori* grounds, the latter alternative has always appeared to the writer highly improbable, that such a variety of molecular species should all originate from a single source by any natural process in a single step either chemical or biological. If, then, a process is conceived by which a whole series of hydrocarbons can be produced from one original member by a succession of steps under such conditions as may exist in nature, such a process must appear to have the higher degree of probability.

We encounter, however, the difficulty that saturated hydrocarbons have not generally been credited with great chemical reactivity toward each other, especially not in the process of building higher from lower ones. If the organic chemist desires to add together two hydrocarbon molecules, he resorts to roundabout and most unnatural processes, such as substituting a chlorine atom in each, then removing the two halogens simultaneously by the vigorous action of a strongly basic metal like sodium, with the object of adding the two free hydrocarbon radicals together.

Since it would be impossible or highly improbable for this kind of synthesis to occur in nature, and if no simpler one could be conceived, an organic origin of petroleum from animal or vegetable sources would be favored, since an initially high molecular weight followed by thermal degradation would be required.

Let us examine the general thermodynamic relations in reactions between saturated hydrocarbons. Generally, they involve but small free chemical energy. For this reason, there is no driving force to cause interaction, and under ordinary conditions they *are* quite inactive toward each other. On the other hand, since there is no driving force in any direction, there is no large opposing force to be overcome; in other words, the heats of reaction are low. Furthermore, if suitable conditions are found to produce reaction, and since there are no large directing forces, one may expect reaction to take place in any direction and to proceed by successive steps in all directions, hence leading to great complexity of product, without having to assume such variety in the original source.

A thermodynamic treatment of possible reactions between hydrocarbons has been recently given by Professor H. A. Wilson[3] of the Rice Institute. Between successive members of the paraffine series in the region of temperatures of several hundred degrees and pressures from a few to several hundred atmospheres he assumes equilibria of the type:

$$2\,C_nH_{2n+2} \rightleftarrows C_{n+1}H_{2(n+1)+2} + C_{n-1}H_{2(n-1)+2}.$$

Thus there exists an equilibrium, dependent on pressure and temperature, between any member of the paraffine series and the members next above and next below in the series in point of number of carbon atoms. Since the relation is perfectly general, it will extend in both directions: to methane, ethane, at the lower, gaseous, end of the series, and to solid members at the upper end. The light gases will be either trapped, and thus furnish the gas pressure associated with petroleum, or, if liberated, will allow the dynamic equilibrium to cause a chemical drift of the hydrocarbons continuously from higher toward lower members.

Professor Wilson has pointed out that so far as his calculations are concerned, the equilibria might be purely physical ones among preexisting members of the series, but it seems quite justifiable to make the step, as he does in his later paper, "Theory of Cracking,"[4] of applying the same considerations to equilibria arrived at by chemical action. To the writer, it appears entirely logical to extend the reasoning to the processes of petroleum generation, regarding cracking and petroleum formation as entirely similar processes from the chemical standpoint, after making due allowances for such differences of physical conditions as would be necessary.

With this kind of mechanism, it would be possible then under influence of such temperatures and pressures as may quite reasonably exist in the earth's upper crust, to start with any member of the paraffine series and arrive at a liquid mixture like petroleum.

The olefine series has been given similar thermo-

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[3] Proc. Roy. Soc. 116A, 501 (1927); 120A, 247 (1928).
[4] Proc. Roy. Soc. 124A, 16 (1930).

dynamic treatment by Professor Wilson.[5] It offers no new difficulties. Equilibria similar to those among the paraffines may be set up. Transition from paraffines to olefines could be effected by the elimination of methane. The treatment promised by Professor Wilson for benzene and the other ring series has not yet been given. It is an interesting question whether a transition from chain to ring members could be accomplished by inorganic processes in nature or whether the ring members originated in life processes in the primary source. While there is some evidence of the generation of benzene derivatives from paraffines by some of the vigorous agents to be next discussed, it is by no means conclusive as yet.

Besides the reactivity of hydrocarbons under the influence of heat and pressure just discussed, other more vigorous agents such as electrical discharge,[6] alpha radiation,[7] and ultra-violet light[8] have been found effective in causing them to interact. While all of the characteristics of these various types of agents are not as yet understood, they have one property in common which is rather surprising. In spite of the large quantum amounts of energy applied, the hydrocarbons are not generally broken down, but exhibit the striking property of condensation to form liquids or solids, with only so much elimination of lower gaseous members as is necessary to avoid chemical supersaturation.

Even when spectrographic evidence indicates an intermediate dissociation of high degree, as in the recent work of Harkins and Gans,[9] subsequent action leads to additional products in solid and extremely inert states.

The preciseness of the results obtained in the action of alpha rays on gaseous hydrocarbons has permitted the development of a theory of the reaction mechanism. Whether it be direct action between ions and molecules or interaction of free radicals does not concern the present discussion vitally. The predominant result is condensation of lower to higher members on up into the region of liquids and solids.[10] The theory gained from the alpha-ray studies also predicts a great variety of products both in the paraffine and olefine series. Starting from a single member either high or low should lead to all other members above and below, distributed according to some form of probability curve with its peak at the member having double the number of carbon atoms of that in the original molecule. The theory is confirmed among gaseous members, but owing to the scant quantity of liquid obtained under alpha radiation, fractionation of the liquid products has not been attempted. However, the same theory has been found applicable to liquids obtained by electrical discharge in hydrocarbons.[11] The quantities of liquid thus obtained have been sufficient to permit of some fractionation. Great complexity is revealed, as expected, and highest abundance for the molecular species with the number of carbon atoms double that of the original species; for example, octane from butane.

The application of some of these processes to the origin of petroleum may appear remote. Indeed it is so, except as the general principle may apply that when a certain type of reactions or a set of products is demonstrated to be possible through the employment of some special agent like ultra-violet light or alpha radiation, the probability becomes greater that some conditions of temperature, pressure or catalysis exist which render the same reactions possible with a lower quantum expense of energy.

Although electrical discharge and ultra-violet radiation are abundant in the earth's atmosphere, they are unknown in the crust and hence can play no rôle in synthesis of petroleum. But, not so with alpha radiation, which, due to the universal radioactivity of the crust, is everywhere present, though in very low intensity. In their original consideration of the chemical behavior of hydrocarbons under alpha rays, Lind and Bardwell pointed out[12] that feeble intensity of radiation might be so compensated by prolonged action through geological periods of time as to suggest a theory of the origin of petroleum from gaseous hydrocarbons under the influence of alpha radiation, provided two apparent obstacles could be overcome. First, are there conditions in the crust under which an appreciable fraction of the alpha radiation could be absorbed by hydrocarbons? Since the "porosity" of gas and oil sands reaches the value of 20 per cent., it seemed probable that the fraction of alpha radiation effectively absorbed in the petroleum structure might approach that degree of efficiency. The second obstacle appears more formidable. The action of alpha rays on all members of the paraffine and olefine series was found to result in the liberation of much hydrogen; whereas in all natural gases occurring in the United States, hydrogen is notably absent.

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[5] *Loc. cit.*

[6] Lind and Glockler, *J. A. C. S.*, 50, 1767 (1928); 51, 2811, 3655 (1929); 52, 4450 (1930).

[7] Lind and Bardwell, *ibid.*, 48, 1556; 2335 (1926).

[8] *Stan. Tolloczko, Przem. Chem.*, 11, 245 (1927); Taylor and Hill, *J. A. C. S.*, 51, 2922 (1929); *Viktor Kemula, Roczn. Chem.*, 10, 273 (1930).

[9] *J. A. C. S.*, 52, 2578; 5165 (1930).

[10] W. T. Richards, Proc. Camb. Phil. Soc., 23, 516 (1927).

[11] Lind and Glockler, *J. A. C. S.*, 52, 4450 (1930).

[12] *Loc. cit.*

In the purely thermal processes of Professor Wilson, liberation of hydrogen is not assumed. This alone would appear to make his mechanism the more probable. But neglecting this hydrogen difficulty, if we calculate the amount of petroleum in the earth's crust that would correspond to the present total of helium content of the atmosphere, on the basis that each atom originated in the crust as an alpha particle, a large total is arrived at. This calculation has been made by Farr and Rogers[13] on the basis of 100 per cent. efficiency in the utilization of the alpha-ray energy in producing petroleum and assuming the same yield per ion pair as found by Lind and Bardwell experimentally. The estimated total of two billion tons for the Petrolia Field of Texas is so huge that even after making large allowances for overestimation of energy utilization, yield, etc., the balance could still exceed the actual production.[14] Corrections in the opposite direction, such as possible loss of helium from the atmosphere leaving the present total content too low, and helium in natural gases still remaining in the earth would raise the total possible. The calculations of Farr and Rogers also have the advantage of being independent of any time factor. It may be mentioned incidentally that some recent analyses of natural gases in New Zealand by the same authors report as much as 4 to 20 per cent. of hydrogen in ten out of eighty-two samples, though the helium content in none of them exceeded 0.02 per cent.

To sum up, it may be said that we now know processes either thermal or ionic by which progression both up and down the hydrocarbon series is effected, starting from any member in the series. This leads directly to the complexity found in natural petroleums, as is also found in the electrically synthesized ones. Consequently, the starting material, whether of vegetable, animal, or mineral source, does not need to be a complex mixture, but may be a single chemical species, from which a high degree of complexity is obtained by steps which appear simple and natural when the chemical and thermodynamic properties of hydrocarbons are taken into account. The simplicity of such a mechanism may lend indirect support to the old idea of an inorganic origin from one or a few hydrocarbon gases such as might be produced by the action of water on metallic carbides in the earth's interior. On the other hand, it does not preclude animal or vegetable origin, but strongly suggests that the primary material, whether gaseous, liquid or solid, is later subjected to thermal (or ionic) agents (or both) which produce the complexity found in nature.

SOME RECENT ASPECTS OF NEMATOLOGY[1]

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ZOOLOGICAL text-books give nemas inadequate treatment—treatment altogether disproportionate to their scientific and practical importance; the space devoted to nemas is insufficient, while many of the statements are antiquated and erroneous.

In judging this defect about 250 zoological and biological text-books printed in English were examined, including text-books proper and books often recommended to students for collateral reading.

A review of these books arouses the suspicion that the text-book treatment given the nemas instead of improving has retrograded. Certain text-books of fifty years ago, now no longer used, give this phylum better treatment than is often the case with texts of to-day.

To cover recent practice it was decided to examine carefully only latest editions. These were grouped, 32 of zoology, and 28 of biology. As a definite basis of comparison seemed necessary, it was decided to compare the nemas with the echinoderms and with the protozoa—a selection determined in part by the following consideration. A cursory examination showed that very much more space is given the echinoderms than the nemas. Since both groups are regarded as phyla and since the two groups present something near the same degree of complexity of organization and since both have long been known to science, it was thought they would furnish material for an illuminating comparison. Reasons for comparison with the protozoa will be presented later.

The percentages of text-book space given the phyla were compared, as well as the number and quality of the illustrations. The percentage of space occupied in each case was taken as a basis of comparison in order that the size of the page and of the type might safely be disregarded.

The 32 text-books of zoology devoted, on the aver-

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[13] *Nature*, 121, 938 (1928); M. N. Rogers, *New Zealand Journ. Sci. and Technol.*, 11, 389 (1930).

[14] It is also to be remembered that only about 20 per cent. of the oil contained in a structure is actually recovered.

[1] Extract from the 1929 presidential address before the American Society of Parasitologists, American Association for the Advancement of Science, Des Moines, Iowa.