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MECHANISM OF THE FORMATION OF SHALE OIL ISOPRENOID ALKANES

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Taking into account differences in thermal stability of various C-C bonds in phytol radicals, it has been demonstrated that all the regular isoprenanes present in shale oils may originate from iC_{20} substituents in the shales organic matter.

In addition to aliphatic hydrocarbons (HC) of normal structure, saturated regular isoprenoid hydrocarbons with chain length of 12 to 20 have been identified in the semicoking oil from the debitterized Selennyakh shale of northeastern Yakutia. The Selennyakh shale kerogen contains a substantial amount of these isoprenoid structural elements. The isoprenoid alkanes constitute 64.3 % of the C_{12} - C_{20} n -alkanes and 39.1 % of total n -alkanes in oil. Figure 1 depicts the distribution of n -alkanes, n -1-alkenes and isoprenoid HC of the oil under study according to the chain length (starting from C_{12}). It is evident from this Figure that the concentration of isoprenoids changes with a specific pattern.

Either the alkyl substituent of isoprenoid structure in kerogen has the specific corresponding length or the composition of isoprenoid HC in semicoking oil is established by peculiarities in the thermal decomposition of the phytol part of the chlorophyll (the major source of isoprenoid

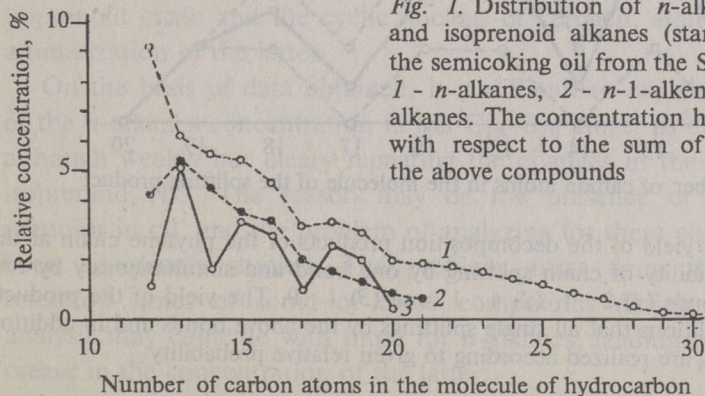
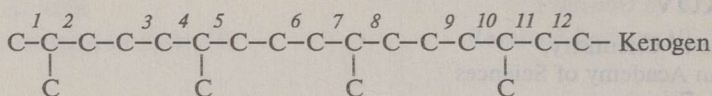


Fig. 1. Distribution of n -alkanes, n -1-alkenes and isoprenoid alkanes (starting from C_{12}) in the semicoking oil from the Selennyakh shale. 1 - n -alkanes, 2 - n -1-alkenes, 3 - isoprenoid alkanes. The concentration has given as relative with respect to the sum of concentrations of the above compounds

fractions in kerogen, incorporated into its structure in some form) our problem is in defining whether the splitting of the *i*-C₂₀ chain occurs during a kerogen formation stage or by its thermal decomposition during processing.

The following structure is presented: an isoprenoid structural element of kerogen in the form of a saturated phytyl radical which is bound to the cyclic skeleton of kerogen by means of a carbon-carbon bond. (The Sellenyakh shale underwent noticeable catagenesis and the preservation of ester and unsaturated aliphatic bonds in its kerogen is improbable.)



As a likely variant, it is suggested that bonds 3, 6 and 9 are thermally the most unstable C-C bonds in the main chain. These correspond to the depolymerization of phytane as a natural polymer. Bonds 1, 2, 4, 5, 7, 8, 10 and 11 (at tertiary carbon atoms) and bond 12 (in the β -position to the cyclic nucleus of kerogen) also split more easily (in the case of considerable aromatization, which is really the situation in the present case), than the adjacent α -bond.

Figure 2 illustrates the distribution of the decomposition products of the phytane side chain. They are presented according to the number of carbon atoms (in the C₁₂-C₂₀ range). This assumes that the splitting of all the aforementioned bonds is equally probable. But the probability of chain splitting by one carbon-carbon bond is different than the probability

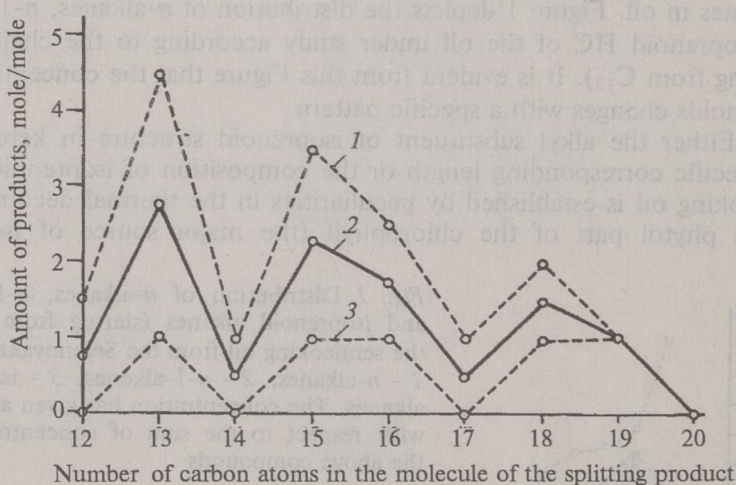


Fig. 2. Calculated yield of the decomposition products of the phytane chain at the ratio of the probability of chain splitting by one bond and simultaneously by two carbon-carbon bonds (1) 2 : 1, (2) 4 : 1 and (3) 1 : 0. The yield of the products has found at conditions that all single splittings by the above bonds and in addition - double splittings are realized according to given relative probability

for simultaneous splitting of two bonds, or successive splitting of two bonds during the same process. The distribution of decomposition products in the case where chain splitting occurs in one bond is four times as probable as simultaneous splitting of two bonds (that is in agreement with the current understanding of the chemistry of thermolysis at moderate temperature in an open system) and corresponds well with the actual distribution of isoprenoid HC in the oil under study (Fig. 1).

Consideration of other variants (equally probable cleavage of all C-C bonds in the chain, splitting of chains at tertiary carbon atoms only, depolymerization of the chain to monomers, etc.) led to distribution of decomposition products which is clearly different from the actual results.

Thus, practically the entire set of shale oil isoprenoid HC may be explained by the cleavage of the phytyl radical at the aforementioned bonds, and there is agreement between the calculated results and the experimental data, proving the existence of such a mechanism.

When estimating the quantity of chains of isoprenoid structure in a kerogen, one should consider that the regular isoprenoid alkanes C_{12} - C_{20} usually identified, contain only 45.7 % of carbon of the initial chain, according to the aforementioned scheme (low-boiling products C_5 - C_{11} contain 46.4 %, gases C_1 - C_4 7.9 %).

The reason for the relatively low concentration of isoprenoid alkanes C_{12} and C_{17} in the organic matter of sedimentary rocks has been considered earlier [1]. It is believed that this is due to the difficulty of formation of these compounds. Such a product requires simultaneous cleavage of two C-C bonds of the phytane chain. But the low concentration at i - C_{14} in sedimentary organic matter (which is known to take place [2]) cannot be explained in such a manner. Based on the data of the present work, minimum concentrations of the transformation products of the i - C_{20} chain may be expected with 2, 4, 7, 9, 12, 14 and 17 carbon atoms.

Finally, in the decomposition products an increase in the pristane : phytane ratio (which is considered a distinctive geochemical feature) may be expected as a result of the strengthening of the α -bond between the isoprenoid chain and the cyclic nucleus of kerogen, along with advancing aromatization of the latter

On the basis of data obtained, it is difficult to explain the rhythmicity of the n -alkanes concentration in the C_{14} - C_{20} range, as depicted in Fig. 1, although weakly but clearly repeating the changes in the concentration of isoprenoid HC. The reason may be the presence of unsaturated isoprenoids in oil, and the problem of analyzing for these compounds has not been adequately studied. The problem arises from the fact that the retention times of some of these compounds during chromatographic analysis may coincide with those for n -alkanes, leading to an artificial increase in the concentration of the latter.

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