

## MONOALKYLBENZENES IN OILS OF THE VENDIAN-CAMBRIAN DEPOSITS

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*Peculiarities of the distribution of high-molecular normal alkylbenzenes in the Vendian-Cambrian oils of the Siberian platform are studied according to the data of chromatomass-spectrometry. The predominance of high-molecular homologues with the odd number of carbon atoms in a molecule is established. The possible biochemical precursors and the probable mechanism of the formation of "odd" monoalkylbenzenes are suggested.*

### Introduction

The detailed study of the composition and peculiarities of the distribution of high-molecular aromatic hydrocarbons (HC) is of interest for solving the problems of oil origin and evolution in lithogenesis. Monoaromatic hydrocarbons are very informative in this respect. They belong to the homological series of alkylbenzenes, the content of which in the sum of monoarenes makes from 5 to 25 % [1].

It is established [1-9] that high-boiling alkylbenzenes are represented by hydrocarbons of several homological series of different structure and can contain 2-3 methyl groups and one long chain of the normal and branched structure with a number of carbon atoms up to C<sub>20</sub> and more. Among them there are alkylbenzenes, 1,2-, 1,3-, 1,4-methylalkylbenzenes, 1,3-, 1,4-ethylalkylbenzenes, hydrocarbons C<sub>20</sub> and C<sub>27</sub> with alkyl chains of the isoprene structure. Concentration of alkylbenzenes decreases with the increase in their molecular weight, concentration of para-methylalkylbenzenes being significantly lower than that of the rest di- isomers.

With the increase in temperature and pressure the content of alkylbenzenes changes in the direction of accumulation of components, which are thermodynamically more stable. In their content the portion of n-alkylbenzenes, 1,3-methylalkylbenzenes and 1,3-ethylalkylbenzenes increases due to the transformation of o-isomers to m-isomers, which are thermodynamically more stable.

According to the existing opinion the aromatic HC are not synthesized by the living organisms but are formed from the organic compounds, which they contain, in the process of organic matter transformation due to biochemical and thermochemical

reactions. The presence of trace quantities of polycyclic aromatic hydrocarbons in some representatives of the plant and animal life is caused not by synthesis but by their accumulation in the process of vital functions. The aromatic structures found in the nature relate to the lignin, pigments and essential oils [1, 10, 11].

Unsaturated fatty acids of lipidic components of the living matter are considered to be the biochemical source of high-molecular alkylbenzenes with the unbranched chain. It is suggested that in the process of their dehydration cyclization, occurring on the natural catalysts, and following reactions of destruction, joining of free radicals and decarboxylation the homological series of n-alkylbenzenes is formed. The scheme of the process is as follows: acid – lactone – cetone – hydrocarbons [1 – 3]. According to this scheme unsaturated fatty acids can be the biochemical source of n-alkylbenzenes and of all range of aliphatic, cyclic and aromatic hydrocarbons of C<sub>6</sub>-C<sub>35</sub> composition, which usually are formed during the contact between the fatty acids and aluminosilicates [1]. The above fact allows to speak about the genetic relationship between n-alkylbenzenes, alkylcyclohexanes and n-alkanes.

Therefore, analyzing the above information one can obtain a sufficiently definite concept about the composition and structure of petroleum monoaromatic hydrocarbons, their biological precursors, ways of transformation to oil hydrocarbons and their transformation in reservoirs. Nevertheless, there are some unsolved problems concerning their formation. In the paper considered on the basis of the scientific literature data and own material the author tries to represent her idea of the process of monoaromatic HC formation in the depths, alkylbenzenes with the alkyl chains of a normal structure, in particular. The choice of n-alkylbenzenes is caused by the absence of their analogues in the animate nature and, therefore, the process of their formation must reflect one of the ways of bioorganic matter transformation in the depths.

#### Objects of investigation

The objects of investigation are Vendian-Cambrian oils of the Srednebotuobinsky, Irelyakhsky and Talakansky fields of the Nepsko-Botuobinskaya antecline. Oils of the fields of the Nepsko-Botuobinskaya oil and gas region are characterized by a wide range of physico-chemical factors: density – 821-907 kg/m<sup>3</sup>, paraffin content – from trace concentrations to 4,4 %, sulfur – 0,1-2,0 %, yield of benzene cuts from 7-38 %. The oils differ mainly in methane composition (41-73 %

methane-naphthene HC). Excluding Talakanskaya oil, all the rest oils have a higher content of asphalt-resinous components: resins – to 43 %, asphaltenes – to 11 %.

### METHODS OF INVESTIGATION

The chromato-mass-spectrometric investigation was performed on the device Q- mass-910-Autosystem (Perkin Elmer). HC separation was made with the use of the capillary column with the silicone phase of the PE-5 type. Chromatography was realized in the regime of the linear programming of temperature: the beginning of the program – 40 °C, rate of temperature increase – 5 °C/min, the end of the program – 320 °C. Scanning of the chromatogram by fragmentary ions  $m/z$  71, 82 and 91 (Fig. 1) allows to identify homological series of n-alkanes, n-alkylcyclohexanes and n-alkylbenzenes in the oils considered. Distribution of n-alkanes is analyzed for the preliminary comparison of oils because n-alkanes are widely used HC – biomarkers. HC identification is realized by comparing the obtained individual mass-spectra with the existing spectra in the system library and published data [12].

### DISCUSSION OF THE RESULTS

Mass-fragmentograms ( $m/z$  71, 83 and 91) for all three samples of oils are identical and are discussed below by the example of the Talakansky field oil.

As Fig. 1 and Table 1 show, n-alkylbenzenes are represented by the homological series  $C_{12}H_{18} - C_{23}H_{40}$ , i.e. the unbranched alkyl substituent contains from 6 to 17 carbon atoms. Low-molecular homologues predominate. The sum of HC  $C_{12}-C_{16}$  makes 44,5 %,  $C_{17}-C_{20}$  – 37,9 %. The relative abundance of high-molecular homologues is 17,6 %. Molecular-mass distribution of n-alkylbenzenes is of a bimodal character with maximums at  $C_{17}$  and  $C_{21}$ . Homologues with the odd number of carbon atoms in a molecule dominate among the n-alkylbenzenes  $C_{17}-C_{23}$ . The odd/even coefficient makes 1,90.

N-alkanes are represented by the homological series  $C_{11} - C_{27}$ . The maximum of n-alkanes distribution is at  $C_{15}$  and  $C_{17}$ ; the odd/even ratio makes 1,11. The distribution of individual n-alkanes within the range of  $C_{12} - C_{17}$  is identical to the n-alkylbenzene distribution, but in the high-molecular zone there are some considerable differences.

Along with n-alkanes the 12- and 13-monomethylalkanes are identified, which are considered as “calling cards” of the Eastern Siberia oils.

N-alkylcyclohexanes are represented by the homological series  $C_{11}$ - $C_{23}$ . Low-molecular homologues predominate. The relative abundance of  $C_{11}$ - $C_{13}$  is 56,2 %,  $C_{17}$ - $C_{20}$  – 36,8 %,  $C_{21}$ - $C_{23}$  – 7,0 %. The maximum of n-alkylcyclohexanes distribution is at  $C_{15}$  and  $C_{17}$ . The odd/even coefficient makes 1,27. The character of the n-alkylcyclohexanes distribution is similar to that of the n-alkanes distribution.

Differences in the ranges of homological series of n-alkylbenzenes and n-alkylcyclohexanes as compared with n-alkanes can be explained by peculiarities of oil catagenesis, which caused the destruction of longer alkyl substituents. Predominance of low-molecular homologues in the considered groups of oil compounds demonstrates the plankton-algal character of the initial organic matter.

As it is noted above the maximum in the high-molecular region, which is at  $C_{21}$ , and also a distinct odd/even coefficient are observed only in the n-alkylbenzenes distribution. According to S.B. Ostroukhov [13] the predominance of the n-alkylbenzene  $C_{21}$  can be explained probably by the participation of a certain organic compound of  $C_{21}$  composition in the formation of the above hydrocarbon.

A higher content of “odd” n-alkylbenzenes in the high-molecular region can be explained possibly by a high content in the sea plants of “odd” polyolefins with a straight chain and 1-6 double bonds in the series  $C_{15}$ - $C_{21}$  [11].  $C_{21}$  predominance can be explained by the fact that some types of plankton algae contain only one hydrocarbon – polyolefin  $C_{21}H_{32}$  with six double bonds – heneicosahexaene – 3,6,9,12,15,18 [14]. The latter allows to suggest the scheme of the formation of n-pentadecylbenzene from the above-named hexaene (Fig. 2). Probably the rest odd homologues are formed as a result of cyclization and aromatization of the rest above-said olefins.

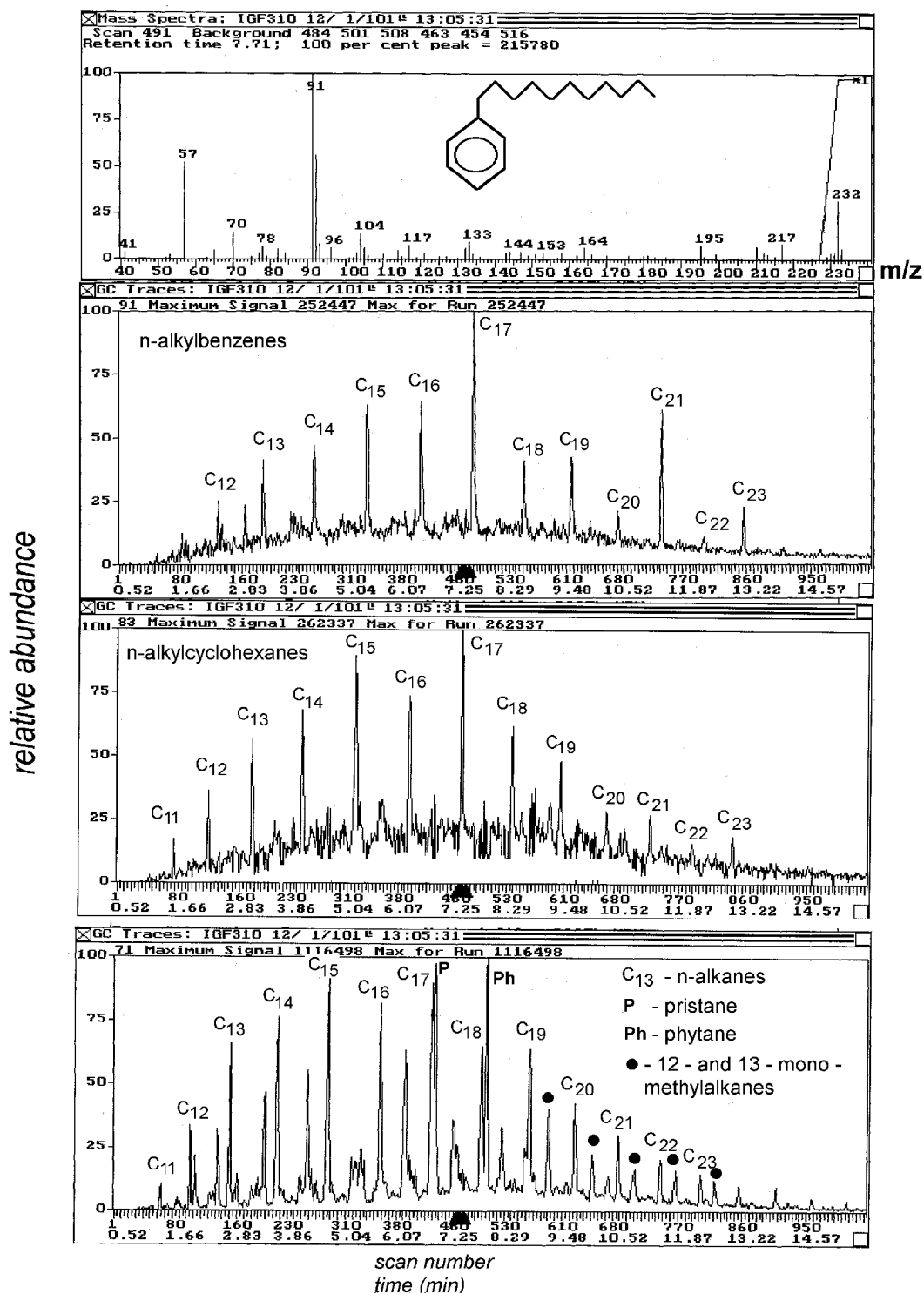


Figure 1. Mass-fragmentograms (m/z 71, m/z 83, m/z 91) of n-alkanes, n-alkylcyclohexanes and n-alkylbenzenes in the Talakansky field oil. At the top one can see the mass-spectrum of n-undecylbenzene.

Table 1

The individual composition of n-alkylbenzenes, alkylcyclohexanes and n-alkanes in the Talakansky field oil

Parameters	Homological series of hydrocarbons		
	n-alkylbenzenes	n-alkylcyclohexanes	n-alkanes
Relative abundance, %			
C <sub>11</sub>		3,24	1,58
C <sub>12</sub>	4,58	5,95	5,18
C <sub>13</sub>	8,50	9,73	9,91
C <sub>14</sub>	8,50	10,81	11,26
C <sub>15</sub>	11,76	14,59	13,51
C <sub>16</sub>	11,11	11,89	11,71
C <sub>17</sub>	20,26	16,76	13,06
C <sub>18</sub>	6,54	9,73	9,01
C <sub>19</sub>	7,84	7,03	8,11
C <sub>20</sub>	3,27	3,24	5,41
C <sub>21</sub>	12,42	3,24	3,60
C <sub>22</sub>	1,31	1,62	2,25
C <sub>23</sub>	3,92	2,16	1,80
C <sub>24</sub>	-	-	1,35
C <sub>25</sub>	-	-	1,13
C <sub>26</sub>	-	-	0,68
C <sub>27</sub>	-	-	0,45
ΣC <sub>11</sub> -C <sub>16</sub>	44,45	56,21	53,15
ΣC <sub>17</sub> -C <sub>20</sub>	37,90	36,76	35,59
ΣC <sub>21</sub> -C <sub>25</sub>	17,65	7,02	10,13
ΣC <sub>26</sub> -C <sub>27</sub>	0,00	0,00	1,13
Maximum	C <sub>15</sub> и C <sub>21</sub>	C <sub>15,17</sub>	C <sub>15,17</sub>
K odd/even	1,90	1,27	1,11

A chain of transformations leading to the formation of high-molecular odd n-alkylbenzenes hypothetically consists of 4 stages.

The first stage: isomerization of heneicosahexaene – 3,6,9,12,15,18. The product of isomerization is the adjoint and thermodynamically stable polyene – heneicosahexaene – 1,3,5,7,9,11. It is known that different adjoint polyenes are capable of the coordinated cyclization either under the influence of light or at heating. As a result of such reaction a double bond vanishes, the other double bonds move and a new simple bond appears between two reaction-capable ends of the adjoint system.

Reactions of such type and reverse reactions (where a cyclic product changes into the acyclic polyene) are called electrocyclic reactions. Since these reactions are reversible, the fact if the reaction proceeds in the direct or inverse direction is determined by thermodynamic factors [15-22].

The second stage: cyclization of the adjoint polyene to cyclohexadiene with the unsaturated hydrocarbon radical.

The third stage: dehydrogenation of the cyclohexadiene ring to the benzene one. The product of change is 1-phenylpentadecatrien-1,3,5.

The last stage: unsaturated substituent recovery; as far as the maturation of the fossil organic matter takes place in the reducing conditions, the n-pentadecylbenzene is formed due to hydrogenation of an unsaturated radical.

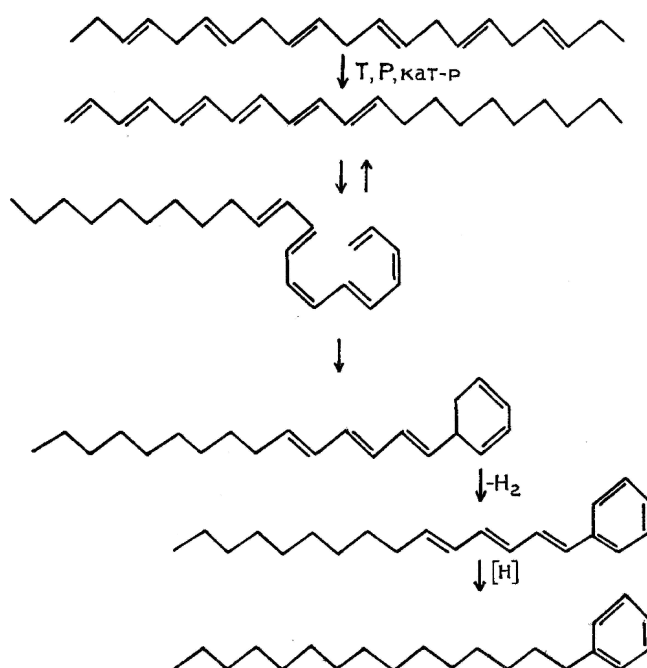


Figure 2. The possible scheme of formation of n-pentadecylbenzene from polyolefin  $C_{21}H_{32}$

## CONCLUSIONS

1. The homological series of n-alkylbenzenes with a distinct predominance of molecules with odd number of carbon atoms in a molecule over even ones in the range of C<sub>17</sub>-C<sub>23</sub> is identified in the oils of the Nepsko-Botuobinskaya anteklise.

2. The author suggests a possible model of forming the odd n-alkylbenzene of C<sub>21</sub> composition (n-pentadecylbenzene) from polyolefin – heneicosahexaene -3,6,9,12,15,18, - the compound contained in the sea plankton algae.

3. The established homological series of n-alkylbenzenes along with the known geochemical peculiarities of oils of the region considered, possibly, suggests either close or common genetic source of hydrocarbon fluids.

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## REFERENCES

1. Petrov A.I. Petroleum hydrocarbons. – M.: Nauka, 1984. – 263 p.
2. Golovko A.K. Petroleum alkylaromatic hydrocarbons // Thesis for a Doctors degree in Chem. – Tomsk, 1977. – 353 p.
3. Golovko A.K., Kontorovich A.E., Pevneva G.S. Geochemical characteristics of oils of the West Siberia by alkylbenzenes composition // Geochemistry. – 2000. – No. 3. – p. 282-293.
4. Korzhov Yu.V., Golovko A.K., Turov Yu.P. Study on the composition of petroleum alkylbenzenes by the chromato-mass-spectrometry // Proceedings of SB AS USSR (Chem. Series). – 1989. – No. 4. – p. 19-24.
5. Ostroukhov S.B., Arefiev O.A., Makushina V.M., Zabrodina M.N., Petrov A.I. Monocyclic aromatic hydrocarbons with the isoprene chain // Petroleum Chemistry. – 1982. – V. 22, No. 6. – p. 723-728.
6. Ostroukhov S.B., Arefiev O.A., Pustilnikova S.D., Petrov A.I. N-alkylbenzenes of the C<sub>12</sub>-C<sub>30</sub> composition in oils // Petroleum Chemistry. – 1983. – V. 23, No. 1. – p. 20-30.



7. Ostroukhov S.B., Arefiev O.A., Zabrodina M.N. Extraction of monocyclic aromatic hydrocarbons from oil // Methods of investigation of the composition of organic compounds of oil and bitumens. M.: Nauka, 1985. – p. 33-40.
8. Gallegos E.J. Alkylbenzenes Derived from Carotenes in Coals by GC/MS // J. of Chromatographic Sci. – 1981. – V. 19. – p. 177-182.
9. Seifert W.K. and Moldovan J.M. Application of Steranes, Terpanes and Monoaromatics to the Maturation, Migration and Source of crude Oils.//Geochim. Cosmochim. Acta. – 1978. – V. 42. – p. 77-95.
10. Tisso V., Velte D. Formation and distribution of oil. – M.: Mir, 1981. - 501 p.
11. Hunt J. Geochemistry and geology of petroleum. – M.: Mir, 1982. – 500 p.
12. Petrov A.I.A., Golovkina L.S., Rusinova G.V. Mass-spectra of petroleum hydrocarbons. Reference book (Atlas). Edited by A.I.A. Petrov. M.: Nedra, 1986. – 313 p.
13. Ostroukhov S.B. On the problem of the origin of oil alkylbenzenes of C<sub>10</sub> composition and higher // Proc. IV Int. Conf. “Chem. Of Petrol. and Gas”. Tomsk, 2000. – V. 1. – p. 349-354.
14. Blumer M., Mullin M.M., Guillard R.R.L. A polyunsaturated hydrocarbon (3-,6-,9-,12-,15-,18-heneicosahexaene) in the marine food web // Mar. Biol. 6 (3). 1970. p. 226-235.
15. Kinney R.E. and Clowley D.J. Pyrolysis of C<sub>2</sub> and C<sub>3</sub> hydrocarbons // Ind. Eng. Chem. 46. 1954.- p. 258-265.
16. Nohara D. and Sakai T. Thermal reaction of 1,5-hexadiene, mechanism proposal // Ind. Eng. Chem. Prod. Res. Develop. 12.1973.- p. 322-325.
17. Nohara D. and Sakai T. Addition reaction of allyl radical and butadiene // Ind. Eng. Chem. Res. 27.1988.- p. 1925-1929.
18. Nohara D. and Sakai T. Kinetic study of model reactions in the gas phase at the early stage of coke formation // Ind. Eng. Chem. Res. 31. 1992.- p. 14-19.
19. Shabarov Yu.S. Organic Chemistry. M.: Chemistry, 1996. – 496 p.
20. Terney A. Modern organic chemistry. M.: Mir, 1981. – 682 p.
21. Berezin B.D., Berezin D.B. Course of modern organic chemistry. School-book for Institutes of Higher Education. M.: Higher School, 1999. – 768 p.
22. Kim A.M. Organic chemistry. Novosibirsk: Sib. Univ. Publishing House, 2001. – 814 p.