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Molecular model of Estonian kukersite kerogen evaluated by ^{13}C MAS NMR spectra[☆]

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Abstract

The chemical structure of Estonian kukersite kerogen is evaluated using a simulation of ^{13}C MAS NMR spectrum. A reasonable fit to the experimental NMR spectrum is obtained by assuming a model of the geomacromolecule with empirical formula $C_{421}H_{638}O_{44}S_4NCl$ and a set of structural elements comprising mainly alkylated phenolic structures particularly alkyl-1,3-benzenediols and condensed alicyclic rings. From the presented model new views are coming up on the carbon skeleton of kerogen and constraints on the phenol formation pathways in the retorting process, i.e. up to 80% of methylene groups in kerogen are located in aliphatic chains and the complicated mixture of phenols in the retort oil seems to result mainly from the thermal conversion of alkyl-1,3-benzenediol units originally present in kerogen.

Keywords: Kerogen; ^{13}C MAS NMR spectroscopy; Molecular modeling

1. Introduction

The modeling of molecular structure of kerogens comprising the relative importance of different nuclei, bonds and functions [1] is a useful tool for the analysis and representation of available knowledge on the constitution and reactivity of these complex geomacromolecules, comprising noncrystalline solid materials insoluble in organic solvents [2–5]. The molecular size and information capacity of these models depend on the available data ranging from some characteristic structural elements to a very complex set of these elements with the molecular masses up to 25,000 D.

The Estonian kukersite kerogen (further kerogen) is classified as a marine kerogen derived from extinct microorganism *Gloeocapsomorpha prisca* [6]. Years ago secondary phenol ethers [7] and a set of methylene chains, alicyclic/benzene rings and oxygen functions [8] were assumed to be characteristic structural units of this kerogen. Very recently Blokker et al. [9] proposed a generalized structure of the *n*-alkyl-1,3-benzenediol based polymer composing the *G. prisca* microfossils which have been isolated from kerogen. However, a consistent model comprising whole bulk structural and molecular information on the kerogen structure is so far lacking. In the present article we are trying to fulfill this gap.

2. Design of the model

2.1. Selection of a number of molecules in the model to be designed

Although kerogen comprises structured component, remains of *G. prisca* and the amorphous part, it behaves chemically mainly as the homogeneous matter [10]. The amount of extractable material from kerogen is very low (<1%). Therefore an assumption was made that at the current stage of knowledge one single molecular model would represent the whole kerogen.

2.2. Initial selection of a set of structural units

Guided by the quantitatively determined aromatic carbon types (Table 1 [11], see quantitation of NMR spectra in Ref. [12]) and based on the results of flash pyrolysis [13],

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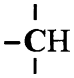
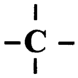
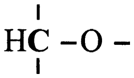
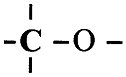
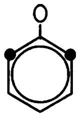
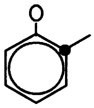
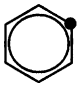
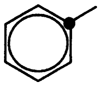
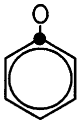
Table 1
Structural units and relative intensities of corresponding lines in ^{13}C CP MAS-NMR spectra of Estonian oil shale kerogen [11]

Structural unit	Location	Chemical shift (width) ppm	Relative area (%)
Methyl	$-CH_3$	13.7(4)	1.4
		21.6(5)	1.6
Methylene	C_2	22.6(3)	1.1
	$-CH_2-$	30(7)	28.2
Methine	 $-\overset{\vert}{\underset{\vert}{C}}H$	31(20)	38.2
Quaternary	 $-\overset{\vert}{\underset{\vert}{C}}-$	39(7)	0.8
			Total **71.3**
Oxy-methylene	$-H_2C-O-$		
Oxy-methine	 $H\overset{\vert}{\underset{\vert}{C}}-O-$	76(17)	4.5
Oxy-quaternary	 $-\overset{\vert}{\underset{\vert}{C}}-O-$		
			Total **4.5**
Ortho-oxyaromatic protonated		108(13)	5.1
Ortho-oxyaromatic branched		118(13)	3.0
Aromatic protonated		126(11) 137(16)	2.4 3.0
Aromatic branched		141(11)	3.9
Oxy-aromatic		155(7)	4.3
			Total **21.7**
Carboxyl	$-COOH$	174(16)	1.3
Carbonyl	$>C=O$	210(13)	1.2

The following conditions and precautions suggested for the routine quantitation of NMR spectra of low aromaticity kerogens [12] were used: CP contact time 1 ms, CP spectrum was quantitatively close to the spectrum recorded without CP technique, spectra of model compounds gave almost correct aromaticity numbers (Section 2.2).

the composition of phenols in kukersite retort oil [14] and the reactivity of kerogen towards maleic anhydride [15] 17 aromatic (except a triene system) structural elements were selected. These structural units comprised five types of aromatic carbon (plus carbon in double bonds) in necessary proportions. From the number of obtained carbon atoms (102) absorbing in the region of 100–160 ppm of NMR spectra and using the correction coefficient 1.1 obtained from the aromaticity ratio of the model alkyl 1,3-benzenediols [11] the total number of carbon atoms in the model (ca. 420) arises. Keeping in mind the elemental composition (%) of kerogen (C–77.0; H–9.68; O–10.6; S–

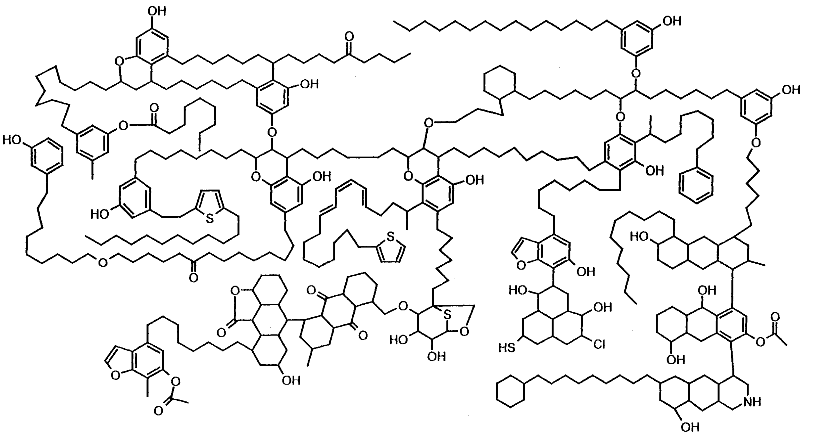


Fig. 1. Designed model of kerogen.

1.7; Cl−0.72; N−0.36) [16]) this amount of carbon atoms results in the model size ca. 6000 D representing all the main elements in kerogen in abundance ≥0.3%. This size is consistent with a rough estimation of molecular mass of the elementary unit of kerogen based on the concentration of spins $10^{16}-10^{17}$ g^{-1} of kerogen [17] representing about one radical per 1000 molecules in polyphenylacetylene-like polymers [18].

2.3. Connection of selected units and the insertion of additional units

The selected structural elements were assembled using mainly aliphatic chains and taking into account the results of oxidative and pyrolytic cleavage of kerogen [9,11,13]. The number of open hydrocarbon chains (5) was obtained from the quantity of chain-end methyl and methylene groups (ca. 1% of the total carbon for both of them). The resulting structure was checked by calculating its elemental composition. The latter forced an insertion of hydrogen-poor cross-links. As the amount of branched hydrocarbon chains is rather low in cleavage products, condensed alicyclic structures were manly used. The role of such structures in kerogen was recognised long time ago [19,20] and demonstrated by the dehydrogenation of kerogen with the elemental sulfur [21]. The molecular information on these structures has been rather poor so far comprising the formation of alkyl- and benzenepolycarboxylic acids upon alkaline $KMnO_4$ oxidation of kerogen [22] and its liquefaction products, respectively, [23]. In case of liquefaction in benzene at 250–300 °C the expected condensed aliphatic structures were probably transformed via hydrogen redistribution into fused aromatic systems resulting in oxidation as a suite of benzenepolycarboxylic acids and giving rise to abundant condensed aromatics in retort oil, e.g. anthraquinone [24]. The latter is the most abundant individual compound separated from retort oil. Based on Refs. [10,25] a sulphurized levoglycosan was inserted and the distribution of oxygen functions in kerogen was taken into account as well [20,26] albeit the latter was modified in accordance with the recent studies. Thus the free phenolic hydroxyl [11] and vicinal aliphatic ether [9] groups were introduced at the expense of arylaliphatic ether and alcoholic hydroxyl groups. As a result, the first candidate for molecular model was obtained.

2.4. Simulation of ^{13}C NMR spectrum

The ^{13}C MAS NMR spectrum of the obtained structure was synthesized using ACD/CNMR™ software package from Advanced Chemistry Development Inc., which calculates ^{13}C NMR spectra for any drawn organic structure. The package includes a large internal database that allows the calculating of chemical shifts with accuracy not exceeding 3 ppm in most cases. In order to recover the discrepancies in chemical shift calculation and to represent the variations of the structure we convoluted the calculated spectrum of discrete lines by a gaussian line of 5 ppm full width, which was found to give the best fit to the main line (methylene groups at 30 ppm) in the experimental spectrum. Then the simulated spectrum was compared to the whole experimental ^{13}C MAS NMR spectrum of kerogen. This procedure was repeated several times changing mainly

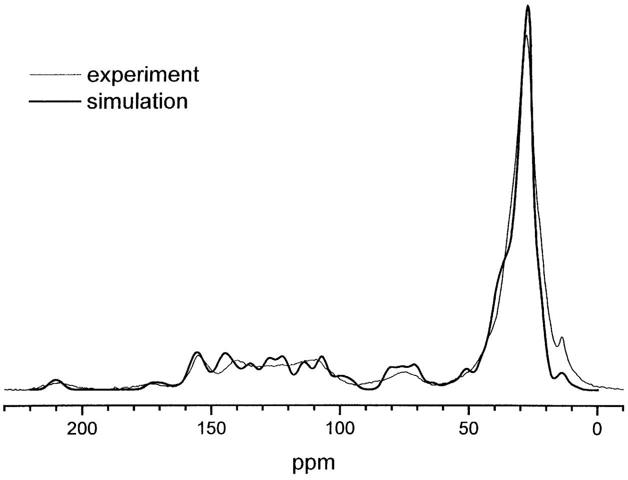


Fig. 2. ^{13}C MAS spectra of kerogen and model.

Table 2
Distribution of aliphatic CH_n carbon (1) and oxygen functionalities (2) in the model of kerogen

(1)			(2)		
Structural unit	Location	Percentage	Structural unit	Location	Percentage
$-CH_3$	Chain end	1.6	$-OH$	$C_{ar}-OH$	22.7
	Cycle, ester	2.6		C_a-OH	20.5
$>CH_2$	Chain	61.9	$-O-$	$C_{ar}-O-C_a$	20.5[a]
	Cycle	12.6		C_a-O-C_a	9.1
$\geqslant CH$	Chain	4.2	$-C(O)O-$	Chain	13.6
	Cycle	16.8		Cycle	4.6
$>C<$	Cycle	0.3	$>C{=}O$	Chain, cycle	9.0

Elemental composition (%): C–76.8; H–9.77; O–10.7; S–1.95; Cl–0.54; N–0.21; empirical formula: $C_{421}H_{638}O_{44}S_4NCl$; molecular mass: 6581 D.

[a] Plus $C_{ar}-O-C_{ar}$.

the structure of alicyclic elements until the necessary fit with the experimental spectrum and elemental composition was obtained. The final structure, its NMR spectrum and this of kerogen, elemental composition and the distribution of functions are given in Figs. 1 and 2, and Table 2.

3. Discussion

3.1. ^{13}C MAS NMR spectrum

We have selected the aromatic molecular units determined mainly by a flash pyrolysis comprising the aromatic carbon types in spectroscopically determined proportions. If the following assumptions—(1) the selected structural units are representative for the whole aromatic part of kerogen, (2) the low molecular compounds in the solution can be used to model the chemical shifts of the similar carbon types in the solid amorphous kerogen—were valid, we ought to observe a good fit of experimental and simulated spectrum. Indeed, in general, a relatively good fit of experimental and simulated spectrum in the region of aromatic and indistinguishable from them olefinic carbon resonances was followed. The coincidence of resonances between 150 and 160 ppm (mainly hydroxylated and oxyalkylated aromatic carbon in 1,3-benzenediol nucleus) is even more amazing keeping in mind the humps of unresolved complex mixtures on the flash pyrolysis chromatograms. The quantitative comparison of aromatic carbon types in the present model of kerogen and these of structure of the polymer composing the *G. prisca* microfossils [9] is shown in Fig. 3. In the latter, one can see, the content of oxyaromatic carbon is ca. twofold overestimated.

The region of resonances caused by the aliphatic carbon attached to the oxygen atom (65–90 ppm, primary/secondary ethers and alcohols) in the simulation spectrum is too 'specific' in comparison with that of kerogen and there are no data for a better choice of these carbons. However, the abundance of this carbon (ca. 5%) reflects well that of kerogen (Table 1). It is necessary to note that according to our experience the distinction between carbons (independently from there valence state) in kerogen linked to hydroxyl and ether groups is not reliable by NMR spectrum.

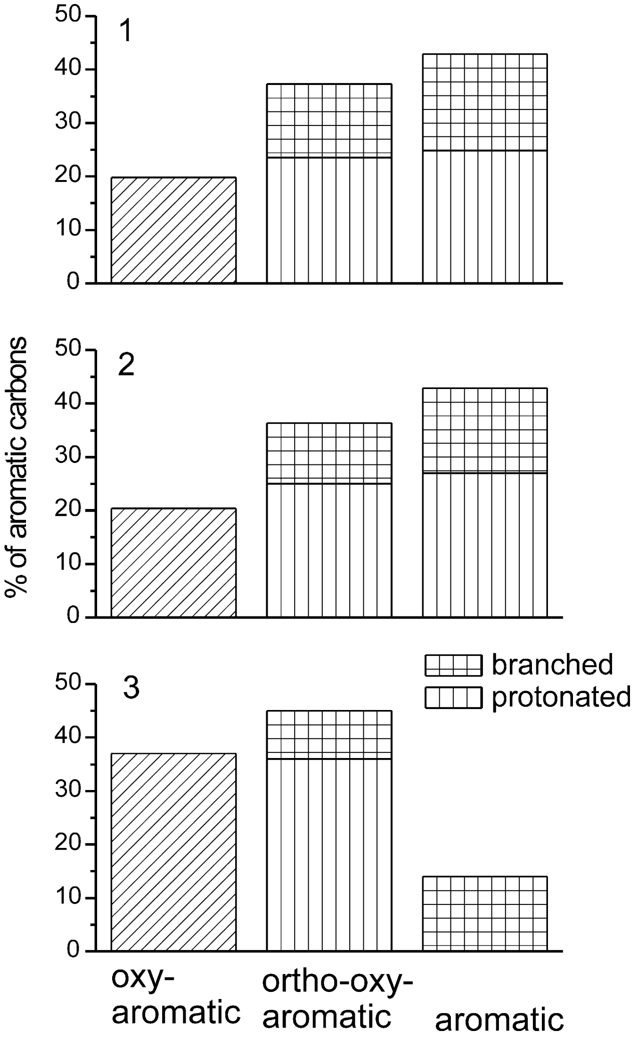


Fig. 3. Comparison of aromatic carbon type composition in kerogen (1), designed model (2) and resistant polymer from *G. prisca* microfossils (3) [9].

The aliphatic resonance manifold (ca. 10–50 ppm) in the simulated spectrum accommodates relatively well the resonances of methylene, methine and methyl carbons among them these of quite arbitrarily chosen cyclic structures. Two types of methyl groups, methylene chain end groups and these attached to aromatic rings and methine carbons are represented as well. Unfortunately no reliable data can be extracted from the spectra to determine the relative abundance of methylene groups in alkyl chains and saturated cycles. So we cannot determine a significant parameter, an average methylene chain length in intact kerogen.

The shown limitations are consistent with data given in Ref. [27] as well. In spite of that the NMR spectra gives a lot of valuable structural information difficult to obtain using some other methods.

3.2. Elemental composition and functionality

Understandably the elemental composition of the model matches relatively well with that of kerogen (Table 2). According to our calculations the biopolymer presented in Ref. [9] consists of up to 79.4 and 10.4% of carbon and hydrogen, respectively, what differs considerably from the corresponding numbers for kerogen.

The model design resulted in the ratio of carbon in aliphatic chains and alicyclic rings ca. 2.2 and it is in accordance with the generalized models of all types of kerogens [2]. Up to 80% of methylene groups are located in aliphatic chains (Table 2). The average chain length is 7.5 methylene groups (the model consisting of 10 methylene groups in an average alkyl chain gave the same result). This is consistent with the carbon numbers of *n*-hydrocarbons [28] and phenols [29] in retort oil. The high ratio of carbon in aliphatic chains and alicyclic rings sharply contradicts the general view on the carbon skeleton of this kerogen based on the interpretation of statistical calculations [20] and kerogen dehydrogenation by using elemental sulfur [21] resulting in the value of mentioned ratio 0.08–0.62. Our model design showed that a different interpretation of the elemental composition is possible as well.

From the intensities of oxygen-bound carbon atom resonances one can estimate the upper limit of O/C ratio in kerogen equal to 0.13. The elemental composition reveals the value of 0.10. The difference is explained by the presence of ca. 25–30% of etheric oxygen (from the total oxygen) [30] which is consistent with the data in Table 2. The distribution of oxygen (% of total oxygen) in hydroxyl, ether, ester plus carboxyl and carbonyl groups of the model structure is 43, 29, 18 and 10, respectively. However, the general coincidence with the known data performed by chemical methods is only apparent (Section 2). In this connection we note a growing evidence of limitations on the chemical functional group determinations in kerogens [11,31].

3.3. General features of reactivity

Concerning the reactivity parameters it is logical that the designed structure will more or less show the features one had put into it, i.e. characteristic pyrolytic and oxidative cleavage products. Likewise it predicts qualitatively general properties of kerogen, e.g. the presented organic material is fully oxidizable with alkaline $KMnO_4$ into low molecular products not comprising in these conditions stable oxygen-dialkylated 1,3-benzenediol nucleus [11] (the biopolymeric structure in Ref. [9] does not have this property), preferential cleavage of C_{sp3}–O bonds, extrusion of alkyl-1,3-benzenediols and pyrolytic water at first stages of the thermal cleavage. The latter needs some comments. The amount of pyrolytic water, 5% from kerogen at 360 °C [32], comprises all of oxygen bound to aliphatic carbon including oxygen in a mixed ether type (Table 1). The point is that due to the deficit of oxygen bound to aliphatic carbon condensed phenolic structures (dioxynaphthalins, heterocyclic phenols, etc. consisting of various homological series with empirical formula C_nH_{2n-z}, where $z = 2–14$ determined by MS group analysis) abundant besides the alkyl-1,3-benzenediols ($z = 2$) in the retort oil [29] obviously cannot be formed via aromatization of cyclic aliphatic alcohols as supposed in Ref. [21]. This is consistent with the views expressed in Ref. [33]. In the light of designed model the total complex mixture of phenols with empirical formula $C_{20.0}H_{26.9}O_{2.6}$ separated from the retort oil in ca. 25% yield seems to be formed via thermal transformations of phenolic structures originally present in kerogen, i.e. mainly alkyl-1,3-benzenediols. This is consistent with the nature of thermal conversion of model alkylbenzenediols [34] and composition of asphaltenes separated from the liquefaction products of kerogen (60% from kerogen) [35]. Keeping in mind the multiplicity and complexity of thermal reactions this question is not discussed here because the initial data of this model simply do not allow it.

4. Final remarks

The relatively low capacity of the model (1109 atoms) forced us to ignore many details, e.g. alkyl chains longer than 15 carbon atoms. Keeping in mind the further design of the corresponding three-dimensional structure with molecular simulation methods the model size is limited by the computational possibilities. Moreover, the more carbon atoms contain the designed model, the more one is forced to include arbitrary aliphatic condensed structures. Concerning the latter, the evergreen question about the ratio of primary/secondary reactions always arises introducing a factor of uncertainty. Strictly speaking only the products of flash pyrolysis can be considered as a proof of the certain molecular structure. However, the latter data are mostly, in best case, half-quantitative and the identified individual compounds comprise only a minor part of the whole kerogen. Therefore it seems that at the current stage of knowledge it is not rational to increase the molecular mass of the presented structure.

While ^{13}C MAS NMR spectrum is a bulk criterion of carbon types, the use of this well-defined parameter has restricted the borders of structural element selection and this way has increased the reliability of proposed ramifications of structural information. Understandably the essence of this work is not the details of the structure on Fig. 1 but the whole emerged consistent picture and the conclusions drawn from it.

The evaluation of available data in the process of model design has led to the new views on the carbon skeleton of kerogen, to the restriction of possible pathways of formation of phenolic compounds and has pointed to the gaps in our knowledge on the kerogen structure. Further research into carbon cross-links, oxygen functions and kinetics of thermal cleavage is necessary to gain new information on the structure of kerogen. In this respect the use of more powerful research methodologies available for soluble geomacromolecules, e.g. bitumens, [36] combined with liquefaction in supercritical solvents [5,37] is promising.

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