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ON THE ORIGIN OF 5-ALKYL-1,3-BENZENEDIOLS IN THE RETORT OIL OF ESTONIAN KUKERSITE

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A historical perspective of the research on the genesis of Estonian kukersite kerogen, the origin and composition of phenolic structures in its retort oil has been briefly given. The plausible origin of 5-alkyl-1,3-benzenediols as an unspecific biological marker, released during the retorting process into oil, has been discussed.

The impetus to write this short review was given by an article [1] published in *Oil Shale* recently. In the article mentioned the research on the genesis of 5-alkyl-1,3-benzenediols in the Estonian shale oil is shown on the confused historical background and the article consists of wrong interpretation of experimental facts.

The most detailed hypothesis of the genesis of Estonian kukersite kerogen (further kerogen if not stated otherwise) has been proposed by H. Raudsepp in the 1950s ([2] and references therein). In accordance with this hypothesis the kerogen is believed to be formed from the lipidic component of the original biological material, comprising all marine organisms living at that time. A special role was given to unsaturated carboxylic acids. The droplets of carboxylic acids in water ("oil in water" model) are transformed through complicated sequence of reactions into macromolecular kerogen.

The cornerstone of this hypothesis are the reactions of oxidation with molecular oxygen responsible for the character of the formed kerogen. Phenolic structures are represented in the kerogen mainly as ethers. In the retorting process these ether bonds are cleaved off and the complicated mixture of phenols consisting of "all aromatic oxy-compounds boiling in the given temperature range" was believed to be formed (up to 20 % on the kerogen) ([3] and citations therein). The presence of ether bonds was demonstrated by HJ and AlBr₃ treatment of the kerogen at 175 and 100 °C, respectively [4, 5]. The absence of reactivity towards diethylsulfate and moderately active *p*-nitrobenzene diazonium ion in carefully selected conditions suggested the presence of phenolic structures with protected hydroxyl groups in the kerogen. The

presence of the latters was indicated also in the reaction with highly activated diazonium ions like *p*-diazobenzene diazonium ion [5].

Nearly at the same time A. Fomina ([6] and references therein), oxidizing kerogen with diluted nitric acid at 105 °C, could not detect aromatic nitroproducts and concluded the absence of phenolether structures in the kerogen. Oxidation with permanganate in the basic media accounted for ca two third saturated carbon atoms from the total carbon. She suggested the role of carbohydrates in the formation of kerogen ("watery humus" model) and the formation of phenols in the retorting process from levoglycosane-like structures. However, years later the same author demonstrated an absence of dibasic phenols, characteristic for the Estonian shale oil [3], in the retort oil of mixtures of agar and linseed oil [7].

From the studies of the dehydrogenation of the kerogen with elemental sulfur a compromise between these two extremes arose and hydroaromatic alcohols were proposed as possible precursors of phenols [8].

The general feature of both aforementioned models is the participation of the corresponding constituents of all organisms, living at that time, in the formation of kerogen.

In the 1960s Ü. Lille ([9-12] and references therein) and co-workers established the preferential content of 5-alkyl-1,3-benzenediols (5-alkylresorcinols) in the retort oil of kukersite (ca 8 % on the kerogen), represented as homologous series from 1 to 17 carbon atoms in the alkyl chain with carbon atom preference 13, 15, 17 in the latter region. This fact, established by wide use of spectral methods and synthesis of pure reference substances, gave to the problems of utilization and genesis of these phenols a new dimension. 5-Alkyl-1,3-benzenediols have distinct chemical reactivity (especially in strongly basic media) and specified biosynthetic pathway in living organisms.

Based on the structural similarity of 5-alkyl-1,3-benzenediols derived from the kerogen to those from plants and microorganisms β -polyketomethylene chains in enol and associated forms were proposed as the hypothetical precursors of 5-alkyl-1,3-benzenediols in the kerogen. We note that the deficit of benzene nucleus in the kerogen to form all aromatics in the retorting products was at that time generally accepted. However, our attempts of thermal cyclization of β -triketones to benzenediols failed - at 100 °C the triketones were stable, at 150 °C the corresponding γ -pyrones were formed in good yield [13]. Complete quotation of this research has been given in [14].

In the late 1970s E. Lippmaa [15] and co-workers registered the ¹³C NMR spectrum of kukersite in the solid phase in which the aromatic carbons particularly these with oxy-substituent are clearly seen (155-165 p.p.m. for the latters). The content of the total aromatic carbon can be estimated 18-20 %, the carbon in the carboxyl groups (with traces of carbonyl) less than ca 3 % from the total (see [16] for quantitation of CP/MAS spectrum). In general this is consistent with the i.r. spectrum of the kerogen as well [17, 18]: characteristic absorption ca at 3500

(/alcoholic/hydroxyl groups), 2950, 1480 (methylene groups), 1750 (carboxyl and carbonyl groups), 1620-1650 (1,3-dioxysubstituted benzene nucleus), 1000-1275 cm^{-1} (ether linkages). Remarkable that 5-alkyl-1,3-benzenediols have the same absorption at 1600-1620 cm^{-1} , the strongest absorption in 680-1750 cm^{-1} region of the spectrum of benzenediols separated from the oil in 13 % yield [14].

Later I. Klesment modified the above mentioned "oil in water" model of kerogen formation and advocated intensively for the presence of poly- β -carbonyl structures in the kerogen and retort oil [19-21]. However, to our best knowledge there is not any correct evidence confirming the essential role of poly- β -keto-methylene chains neither in kerogen nor in the retort oil. Apparently the conclusion [1] that in the kukersite exists an "oxo-enol equilibrium of resorcinol structures" - is not consistent with physico-chemical properties of the intact kerogen (for example, heating of the kerogen by 150°C during 800 hours in a sealed ampoule did not cause any increase in absorption by 1715 cm^{-1} , characteristic of carbonyl group [18]).

The low content of benzenecarboxylic acids in oxidation products of kukersite [22] and the absence of phenols in its conversion products in aqueous suspension [20] is caused by the instability of highly activated benzene ring. Of course, one can not rule out the possibility of keto-enol tautomerism in these processes but it is not relevant to phenol ether structures in the intact kerogen. The lack of aromatic nitro compounds in the oxidation products of the kerogen and the presence of those in the oxidation products of the thermobitumen is probably caused by the additionally formed less activated aromatic rings in the latter (from ^{13}C NMR spectrum of asphaltenes separated from the thermobitumen the part of carbon in aromatic rings can be determined ca 30% [14]).

Poly- β -keto-methylene chains, formed classically by condensation of acetate units in a head to tail manner, are precursors of 5-alkyl-1,3-benzenediols in living matter. Such type of condensation is the origin of the designation "polyketides" for all natural products formed via the mentioned pathway [23] (including for example prostaglandins, the metabolites of polyunsaturated carboxylic acids, the research field for last 25 years of the author of this communication [24]).

The dominant organic matter in all oil shales is derived from lipid-rich precursors (recognised as liptinite macerals) and from this point of view oil shales are related to polyketides. In accordance with the petrographic classification kukersites are designated as marine oil shales principal liptinite of which is derived from microalgae *Gloeocapsomorpha prisca* [25]. (The term "kukersite" originates from Kukruse village in Estonia. So the kerogen of Estonian oil shale is formally the "parent" kukersite). The *G. prisca* was related to the extant freshwater colonial microalga *Botryococcus braunii* and phenolic moieties were demonstrated in its colonies (absorption at 3400 and 1600 cm^{-1} in the transmission-micro-FT-i.r. ([26] and references therein).

To the point, the general features of the presented spectrum are quite similar to those of the spectrum registered for the kerogen. In the

opinion of the authors of the mentioned article the phenolic moieties of kukersites correspond to important basic structures of the resistant macromolecular material building up the thick outer walls of *G. prisca* colonies. These walls are selectively preserved during diagenesis and thus make a major contribution to the kerogen of all kukersites (this hypothesis of genesis of kukersitic kerogens can be termed as "preserved biopolymer" model, it is close to the views expressed by M. Zalesky as early as in 1917 [27]).

We note that 5-alkylated 1,3-benzenediols have been isolated from several species of extant algae (see [28] and references therein) among them corresponding alkyl-aryl ether from *Botryococcus*. However, scanning electron microscopic studies of microfossil-rich part of Estonian kukersite has shown that morphostructural units of different chemical structure are present in the disintegrated kerogen particles and no microfossil structures referable to the green alga *Botryococcus* were revealed [29]. It follows that the biological affinity of *Gloeocapsomorpha prisca* remains unclear (see [30] as well). Combined studies using modern petrographic, spectral and chemical methods are needed to clarify the nature of microfossil and phenolic moiety structures in the kerogen.

This short communication is not aimed at the full analysis of genesis of kukersitic kerogens. May be different mechanisms of kerogen formation have been operating causing structural heterogeneity of the kerogen. However, probably serious corrections are necessary as for the genesis of the Estonian kukersite. In regard to the origin of 5-alkyl-1,3-benzenediols in the Estonian shale oil, the preservation of 1,3-dioxy-5-alkylsubstituted benzene nucleus, arisen from intramolecular condensation of extended poly- β -keto chains in original organism, as the structural element of highly resistant biopolymer component of the kerogen, seems to be very plausible. Such tempting simplification can be really true taking into account the presence of the remnants of carotenoids in ancient rocks as old as 450 million years [31] and the role of sorption by mineral surfaces in the diagenesis demonstrated recently [32, and references therein]. See [33], and references therein as well.

According to the basic concept of G. Eglinton and M. Calvin [34], "the term 'biological marker' is being applied to organic substances that show pronounced resistance to chemical change and whose molecular structure gives a strong indication that they could have been created in significant amounts only by biological processes". In accordance with this definition, the characteristic structural unit in the kerogene of Estonian kukersite - 1,3-dioxy-5-alkylsubstituted benzene nucleus - is a biological marker. This marker is released in the thermal degradation process to form corresponding 1,3-benzenediols.

However, the term 'biological marker' is usually used to denote unique biosynthetic products found in relatively low concentrations in crude oils and rock extracts. In fact the acetate pathway is very common and unspecific. In spite of that the content and composition of phenolic compounds in kukersites have certain indicative power, concerning for example the water salinity, as stated in [26]. We use this term in our

context to point to the supposed biological origin of 5-alkyl-1,3-benzenediols in the retort oil of the Estonian kukersite.

Of course, until the further evidence will be obtained to support the statements above, the question remains - does the oxygen in the molecule of benzenediols belong to the original acetate moiety or it is inserted later in regiospecific oxidation process as is supposed according to the modified "oil in water" model. The latter possibility seems to be incredible. We note that oxidation of polyunsaturated carboxylic acids with singlet molecular oxygen, a possible oxidant in the presence of u.v. radiation in low Palaeozoic era [21], resulted only in monohydroperoxyacids [35]. Hopefully new methodologies for determination of the oxygen - isotope composition [36] could give some new data to clarify this question of poly- β -keto-chain processing, including possibly biological and non-biological stages.

(The basic ideas of this communication were presented in the ordinary memorial lecture in December 1995, in Tallinn Technical University, devoted to the birthday of Prof. Paul Kogerman, the founder of the Estonian oil shale chemistry.)

Conclusion

The origin of 5-alkyl-1,3-benzenediols in the retort oil of the Estonian kukersite kerogen is determined by the chemical structure and genesis of the kerogen. The presence of 5-alkyl-1,3-dioxysubstituted benzene nucleus in the kerogen is consistent with the experimental data. The growing evidence is showing the possibility that this structural element as such originates from the starting lipidic material of the kerogen formation.

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