

<https://doi.org/10.3176/oil.2002.2.02>

INVESTIGATION OF KUKERSITE STRUCTURE USING NMR AND OXIDATIVE CLEAVAGE: ON THE NATURE OF PHENOLIC PRECURSORS IN THE KEROGEN OF ESTONIAN KUKERSITE

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Oxidative cleavage of Estonian kukersite kerogen, model 5-alkyl-1,3-benzenediols and their dialkyl ethers under alkaline $KMnO_4$ and ruthenium ion catalyzed oxidation conditions, followed by CP/MAS ^{13}C NMR and GC-MS studies of products, was carried out. Based on the stability of ether model compounds under alkaline $KMnO_4$ oxidation conditions, full oxidizability of kerogen into low-molecular acidic products and similar carbon type composition of $KMnO_4$ treated and intact kerogen, it was assumed that alkylbenzenediols are bound to the kerogen structure via cross-links in alkyl chains (and possibly via aryl-aliphatic monoether bonds as well). Location of free phenolic hydroxyl groups is determined by hydrogen bonds. Earlier determinations of "apparent" aryl-aliphatic ether bonds, using ether-cleaving HI and bulk $AlBr_3$ reagents under severe conditions, were discussed and the action of trimethylsilyliodide and $AlBr_3$ on the model compounds was examined as well.

The presence of phenolic structures in the Estonian kukersite kerogen (further kerogen) especially 5-alkyl-1,3-benzenediols is well established [1, 2 and citations therein]. However the question of how the phenolic structural elements are built into the structure of kerogen is not clear. So far the experimentally best-founded view suggests the role of phenolic alkylethers as main structural elements in kerogen. This view is based mainly on the following properties of kerogen:

- Lack of reactivity towards diethylsulfate in basic media
- Presence of signals at 75 and 155 ppm in the solid-state ^{13}C NMR spectrum
- Reactivity towards selected ether-cleaving reagents (concd HI, bulk liquid $AlBr_3$)

In the cleavage of kerogen upon KMnO_4 oxidation in basic media the aryl-aliphatic ether bonds are believed to be stable, and the phenolic ethers are supposed to remain in the unoxidized residue [3]. Interestingly, more selective ruthenium ion catalyzed oxidation (RICO) in case of prolonged reaction times and high molar cooxidant/substrate ratios degrades aromatic ring smoothly to carboxylic group [4]. On the other hand it is known that the unoxidized residues of permanganate oxidations of kerogen have more or less constant elemental composition close to that of intact kerogen, and the carbon in kerogen can be nearly fully oxidized into aliphatic carboxylic acids and CO_2 [5, p. 122, 145–146], suggesting the cleavage of all rings.

Based on these observations we decided to check the stability of aryl-aliphatic ether bond upon oxidation and tried to demonstrate the increasing concentration of this structural element in the oxidation residue of kerogen. Having reached negative answer on the latter point we tried to get some insight on the stability of a representative free phenol and phenolethers towards AlBr_3 and iodotrichloro- and iodotrimethylsilane, respectively. The latter reagents are modern HI analogues acting under very mild conditions [6].

Experimental

Sample of Kerogen. Flotation concentrate of technological kukersite (92 % of organic matter) was used.

Model Compounds. 5-Methyl-1,3-benzenediol (I) (Institute of Chemistry at Tallinn Technical University), 2-*n*-nonyl-, 5-*n*-decyl-, 2-*n*-nonyl-5-*n*-decyl-1,3-benzenediols (II), (III) and (IV), respectively, originated from the collection of pure alkyl-1,3-benzenediols synthesized via selective metallation of dimethyl ether of (I) followed by coupling with corresponding iodoalkanes and demethylation [7, 8].

Phenol ethers 5-methyl-1,3-dimethoxybenzene (V), 5-methyl-1,3-dihexyloxybenzene (VI) and 5-methyl-1,3-di(1-methyl)heptyloxybenzene (VII) were prepared alkylating (I) with dimethylsulfate in the presence of anhydrous KCO_3 [9], with *n*-bromoheptane and 2-bromooctane in aqueous solution of NaOH in the presence of tetradecyltrimethylammoniumbromide [10], respectively. 1,4-Diheptyloxybenzene (VIII) was prepared by the latter method. Undecanal (IX) originated from Sigma.

NMR studies. Solid-state ^{13}C NMR measurements were carried out in a 4.7 T magnetic field using upgraded Bruker CXP-200 spectrometer and home-built MAS-NMR probehead. The samples were spun at 5 kHz spinning rate in standard 7 mm zirconia rotors. ^{13}C magnetization was enhanced via cross polarization (CP) technique using a contact time of 1 ms. This contact time results in adequate intensity distribution of resonance lines in ^{13}C MAS-NMR spectra of this low maturity kerogen [11]. Our comparison of CP spectrum to the spectrum recorded without CP technique showed no re-

markable differences. Since cross polarization sequence gives better baseline and signal to noise ratio the usage of CP enhanced spectra for quantitative carbon type analysis is generally accepted [11, 12]. The analysis of the spectra can be significantly improved using a second spectrum recorded by the pulse sequence which includes dipolar dephasing (DD) period $t_{DD} = 50 \mu\text{s}$ between the CP pulse and the beginning of data acquisition [13]. In the DD spectrum the resonances from carbons, which are strongly coupled to protons, are almost absent, and only nonprotonated carbons plus mobile methyl carbons contribute to the spectrum.

In order to determine statistical weight of different carbon types in kero-gen we followed the procedure described earlier by Mann *et al.* [11]. According to this procedure we first accumulated ordinary CP/MAS spectrum (Fig. 1), then DD spectrum was obtained from the same sample with the same set-up of the spectrometer. Next we applied a computer fit to the DD spectrum of nonprotonated and methyl carbons using appropriate number of Gaussian lines. Then the DD spectrum was subtracted from the ordinary CP/MAS spectrum. The resulting spectrum of protonated carbons was fitted by another set of Gaussian lines. Statistical weight of different types of carbons was determined as the ratio of the area of certain carbon line to the sum of all lines.

The quantification of spectral data was controlled additionally by the determination of aromaticity ratio (f_a) for model compounds (II), (III) and (IV), which is obtained by summation of the signal due to aromatic carbons divided by the total signal of the CP/MAS NMR spectrum.

The spectrum of (IV) gave $f_a = 22.7 \%$ instead of $6/25 = 24 \%$.

The spectrum of (III) gave $f_a = 42.7 \%$ instead of $6/13 = 46.2 \%$.

The spectrum of (II) gave $f_a = 37.1 \%$ instead of $6/15 = 40 \%$.

These examples show that CP/MAS NMR spectra give almost correct aromaticity numbers, although we note the tendency to get few percent smaller ratio than in reality.

NMR solution studies were performed on a Bruker AMX-500 instrument to check the purity of synthesized compounds and composition of soluble in chloroform products from the conversion reactions.

Elemental Analysis was performed on a Perkin-Elmer 2400 CHN analyzer.

IR Spectral Measurements. IR spectra were obtained in KBr pellets using Hitachi 270-30 instrument.

GC-MS Analysis. Gas chromatograph double-focusing mass spectrometer Hitachi M-80-B. GC column: Alltech AT-5, 30 m, ID 0.32 mm. Temperature programming: 80–300 °C, 12°/min. MS conditions: electron impact, 70 eV, scan range : 0–500 m/e, scanning speed: 1 scan/s. MS libraries: Hitachi M0101 and Benchtop library with 130,000 and 230,000 public reference spectra, respectively.

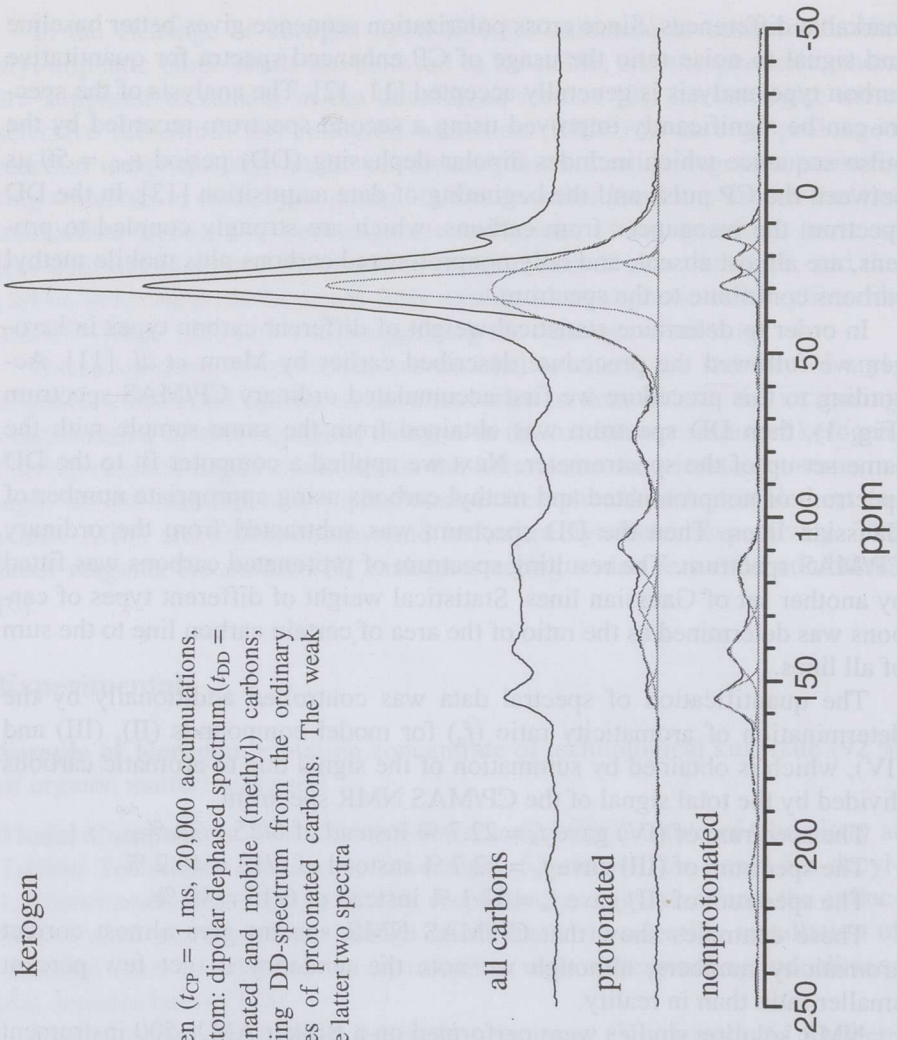


Fig. 1. ^{13}C CP/MAS NMR spectra of kerogen ($t_{\text{CP}} = 1$ ms, 20,000 accumulations, recycle time 1 s). Top: ordinary spectrum; bottom: dipolar dephased spectrum ($t_{\text{DD}} = 50$ μs) contains resonances of nonprotonated and mobile (methyl) carbons; middle: the spectrum obtained by subtracting DD-spectrum from the ordinary spectrum; consequently, it contains the lines of protonated carbons. The weak Gaussian lines represent the computer fit to the latter two spectra

Table 1. Results of KMnO_4 Oxidation

| No. | Reaction conditions | | | | Products, % | |
|-----|---------------------|---------------------------------|----------|----------|-----------------|---------|
| | Substrate, mg | Excess of KMnO_4 , w/w | T , °C | t , hr | Extract | Residue |
| 1 | I (50) | 18 | 95 | 4 | Full conversion | |
| 2 | V (50) | 18 | 95 | 24 | 98** | none |
| 3 | VI (50) | 24 | 75 | 72 | 95** | none |
| 4* | VII (300) | 12 | 75 | 72 | 100** | none |
| 5 | Kerogen (700) | 12 | 75 | 72 | 9 | none |
| 6 | Kerogen (1000) | 4 | 75 | 48 | n.d. | 17 |
| 7 | Kerogen (1000) | 4 | 75 | 48 | 36 | 18 |

* Experiment performed in *t*-BuOH showed similar results.






** Identical to the starting compounds, checked by R_f (V) and NMR data (VI), (VII). Very weak spot with R_f lower in comparison to that of starting material was observed.

Oxidation with KMnO_4 was carried out in one step using conditions as reported in [3]. 0.7–1.0 g of kerogen was stirred in 115 mL of water containing 1 % of KOH and excess of KMnO_4 at 75 °C 48–72 h (Table 1). From the remaining solid residue obtained by filtration, MnO_2 was removed by treatment with an excess of 5 % oxalic acid and 2M $\cdot \text{H}_2\text{SO}_4$ (5 : 1) solution and after drying at 70 °C unoxidized kerogen as dry residue (if remained) was obtained and analyzed by NMR (Table 2) From the solution the acids were extracted with diethylether and dichloromethane. Dried material obtained from combined extracts was methylated with CH_2N_2 and analyzed by GC-MS as shown above. Model compounds (I), (V)–(VII) in amounts of 50 to 300 mg were oxidized similarly using reaction times up to 75 h and 12–24-fold (w/w) excess of permanganate.

RICO was performed as reported in [14]. 100 mg of sample, 2.0 g of NaIO_4 (Fluka 71839), 20 mg RuCl_3 aq (Fluka 84050) in mixture of 4 mL MeCN, 4 mL CCl_4 and 6 mL water was sonificated 3 min and stirred at room temperature 48 h. The acids obtained after work-up (ca 40 wt.% of the kerogen) were methylated with CH_2N_2 and analyzed by GC-MS. The solid residue (130 mg, 22 wt.% of the kerogen) was obtained in a separate 3-fold increased scale experiment carried out twice with oxidation time of 24 h and analyzed by NMR (see Table 1) and CHN analyzer. This residue (elemental composition, %: C – 41.08, H – 5.13, N – 0.08) was fully soluble in pyridine, and in boiling 20 % KOH water solution, less soluble in ethanol. The total amount of acids in this experiment was of 221 mg (37 %). Model compounds (VI)–(IX) in amounts of 10 to 40 mg were oxidized similarly during 48 h [4]. Molar ratio of periodate and substrate 30 : 1 was used.

Treatment with Iodotrichloro- and Iodotrimethylsilane Reagents. Ethers (V)–(VIII) in quantities of a few mmoles were treated with tetrachlorosilane/NaI in toluene/acetonitrile (1 : 1) solvent under reflux 48–72 h and with trimethylchlorosilan/NaI in acetonitrile at 60 °C as described in [6] and [15], respectively.

Table 2. Structural Units and Relative Intensities of Corresponding Resonances in ^{13}C CP MAS-NMR Spectra of Kerogen and of the Solid Residues of Alkaline KMnO_4 and RICO Oxidation

| Structural unit | Location | Kerogen | | MnO_4 treated kerogen | | RuO_4 treated kerogen | |
|------------------------------|---|-----------------------------|------------------|--------------------------------|------------------|--------------------------------|------------------|
| | | Chemical shift (width), ppm | Relative area, % | Chemical shift (width), ppm | Relative area, % | Chemical shift (width), ppm | Relative area, % |
| Methyl | $-\text{CH}_3$ | 13.7(4) | 1.4 | 13.8(5) | 1.4 | 13.9(2) | 0.6 |
| | | 21.6(5) | 1.6 | 21.6(5) | 1.9 | 26.4(17) | 9.1 |
| Methylene | C_2 $-\text{CH}_2-$ | 22.6(3) | 1.1 | 22.6(3) | 1.8 | 23(17) | 20.5 |
| | | 30(7) | 27.2 | 30(8) | 28.6 | 29(9) | 37.9 |
| | | 31(20) | 38.2 | 32(21) | 35.0 | | |
| Methine | $\begin{array}{c} \\ -\text{CH} \\ \end{array}$ | | | | | 42(11) | 15.1 |
| Quaternary | $\begin{array}{c} \\ -\text{C}- \\ \end{array}$ | 29(4) | 1.8 | 29(5) | 2.2 | 29(5) | 2.1 |
| | | | 71.3 | | 70.9 | | 85.4 |
| oxy-Methylene | $-\text{H}_2\text{C}-\text{O}-$ | 76(17) | 4.5 | 76(17) | 5.6 | 76(8) | 1.0 |
| oxy-Methine | $\begin{array}{c} \\ \text{HC}-\text{O}- \\ \end{array}$ | | | | | | |
| oxy-Quaternary | $\begin{array}{c} \\ -\text{C}-\text{O}- \\ \end{array}$ | | | | | | |
| | | | 4.5 | | 5.6 | | 4.1 |
| ortho-Oxyaromatic protonated |  | 108(13) | 5.1 | 107(12) | 4.5 | - | |
| ortho-Oxyaromatic branched |  | 118(13) | 3.0 | 117(12) | 3.6 | - | |
| Aromatic protonated |  | 126(11) | 2.4 | 127(15) | 3.6 | - | |
| | | 137(16) | 3.0 | 143(10) | 1.1 | | |
| Aromatic branched |  | 141(11) | 3.9 | 140(11) | 3.9 | - | |
| oxy-Aromatic |  | 155(7) | 4.3 | 156(7) | 5.2 | | |
| | | | 21.7 | | 21.9 | | 0 |
| Carboxyl | $-\text{COOH}$ | 174(16) | 1.3 | 176(10) | 0.7 | 167(10) | 1.2 |
| Carbonyl | $\text{>C}=\text{O}$ | 210(13) | 1.2 | 211(14) | 0.9 | 178(8) | 5.5 |
| | | | | | | 208(15) | 3.7 |

Treatment with AlBr_3 . Under a N_2 stream 120 mg of (IV) were added to the bulk liquid of AlBr_3 (890 mg, *Soyushkhimreaktiv*) at 100°C and stirred for 30 min. The formation of gas bubbles was observed. After cooling the reaction medium was diluted with water and extracted with CH_2Cl_2 . Extract was washed with water and dried on sodium sulfate. After evaporation of the solvent 65 mg of amorphous material was obtained.

Results and Discussion

“Carbon type” analysis based on solid-state ^{13}C NMR was carried out for characterizing the starting kerogen (see Table 2). Up to 76 % of kerogen carbons corresponds to aliphatic carbons located mostly in methylene groups of alkyl chains and saturated cycles. Unfortunately, these groups cannot be distinguished. Oxygen-bound aliphatic carbons represent 4-5 % and ca 3 % is located in methyl groups. Aromatic carbons represent 20-22 % including nearly equal amounts of protonated and nonprotonated aromatic carbon, carbons in carbonyl and ester functions account for 2-3 %. Noteworthy, the part of nonprotonated aromatic carbon bound to oxygen, ca 4 %, is high enough to explain the presence of abundant aromatic oxygen compounds including phenols in the retort oil. The minor part of olefinic carbons, possibly present in kerogen, cannot be distinguished from the aromatic carbons by NMR. In general, the results of this analysis were explicable in the light of other chemical information not discussed here.

Contrary to the free phenol (I), the primary (V), (VI) and secondary (VII) phenolic ethers were stable upon KMnO_4 oxidation under rather severe conditions (see Table 1). Indeed, atomic oxygen acting as reactive species in permanganate-type oxidation did not cleave aryl-aliphatic ether bond in these model compounds. Oxidation of kerogen under the same conditions did not give any solid residue. It follows that the stable to this reagent aryl-aliphatic ether bond type is not characteristic for kerogen. By shorter oxidation time, ca one fifth of the kerogen remained as unoxidized residue showing NMR spectrum rather close to that of the starting kerogen (see Table 2). It is in agreement with earlier observations that in the alkaline permanganate-type stepwise oxidation the composition of the insoluble residue is close to that of kerogen. This phenomenon can be explained by the high activity of atomic oxygen forming strict reaction front, which causes the “peeling” action of this reagent to kerogen. Such action mechanism excludes the assumed conservation of stable aryl-aliphatic ether bonds in the oxidation residue, which in the presence of these bonds should reach up to 20 % of oxygen-bound aromatic carbon. In fact the slight increase in the intensity of the signals at 76 and 155 ppm remained within the limits of analysis error. However, taking into account the full oxidation of kerogen, the presence of structural units similar to dialkylethers of 1,3-benzenediols is very unlikely.

The signal at 155 ppm seems to be caused by the benzene ring carbons carrying covalently free OH group. This signal cannot be unambiguously distinguished from that of ether-linked aromatic carbons resonating in the same region [16]. Such interpretation is supported by the IR spectrum of kerogen [17] and by the loss of benzenediols in alkaline aqueous conversion of kerogen [18]. The lack of reactivity towards diethylsulfate can be explained by secondary intramolecular interactions in the macromolecule of kerogen, e.g. sterically protected esters inaccessible to hydrolytic attacks were found in torbanite [19]. In coals using vacuum FT-IR four types of hydrogen bonds ordered by thermal stability in the 100–500 °C range were identified [20]. Apparently hydrogen bonds existing in kerogen were eliminated by total trimethylsilylation of hydroxyl groups in kerogen with hexamethyldisilazane/pyridine in sealed ampoule at 150 °C [21]. The release of hydroxyl groups observed upon heating kerogen at 250 °C [22] and the increase of dielectric permeability of kerogen during its bituminization [23, p. 26–27, 46] seem to be the result of H-bond cleavage. We note relatively high bond energy of $C_{ar}-O$ bond (ca 355 kJ/mol) [24]. From the thermolysis re-

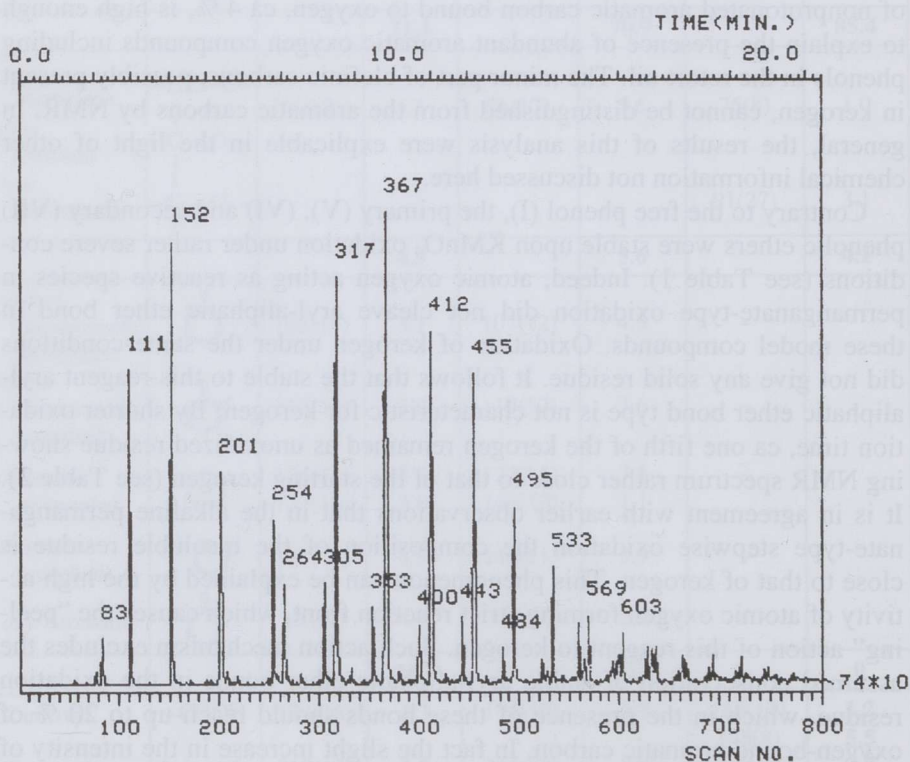


Fig. 2. Mass chromatogram of m/z 74 showing mono- and dicarboxylic acids ($KMnO_4$ oxidation extract). Monoacids: C6 – 111, C7 – 152, C8 – 201, C9 – 254, C10 – 305, C11 – 353, C12 – 400, C13 – 443, C15 – 484; diacids: C6 – 264, C7 – 317, C8 – 367, C9 – 412, C10 – 455, C11 – 495, C12 – 533

sults of (VI) in sealed ampoule at 350–420 °C [25] one can estimate its high stability at 250 °C. Furthermore, unspecified ether functions were identified in pyrolysis residues of torbanite [19].

The signal at 76 ppm is assigned to *oxy*-methine group (aliphatic *sec*-alcohol/*sec*-ether type carbon). Interestingly, this type was found in other algal/bacterial derived kerogens in lesser amounts in comparison to that of linear alcohol/ether type, which is a dominant oxygen-containing carbon type in these kerogens [11]. In the light of the present work the part of ether oxygen in kerogen is considerably less than estimated so far as oxygen in apparent aryl-aliphatic ether bond [26]. It seems that really the action of concd HI on kerogen in sealed ampoules at 175–180 °C resulting in the formation of ether-soluble units of kerogen [27] is more complex than the cleavage of C–O bonds and reduction of aromatic rings. In this connection it can be noted that treatment of *p*-hydroxydiphenyl under the same conditions yielded 40 % of oil boiling in a rather wide range [28].

The composition of the soluble oxidation product showed the usual well-known distribution of di- and monocarboxylic acids (Fig. 2). To our surprise monitoring the mass chromatogram by the m/z 124 ion, characteristic for 5-alkyl-1,3-benzenediols [29], we could observe two close peaks with elution time ca 19 min, scan numbers 682 and 701 (Fig. 3).

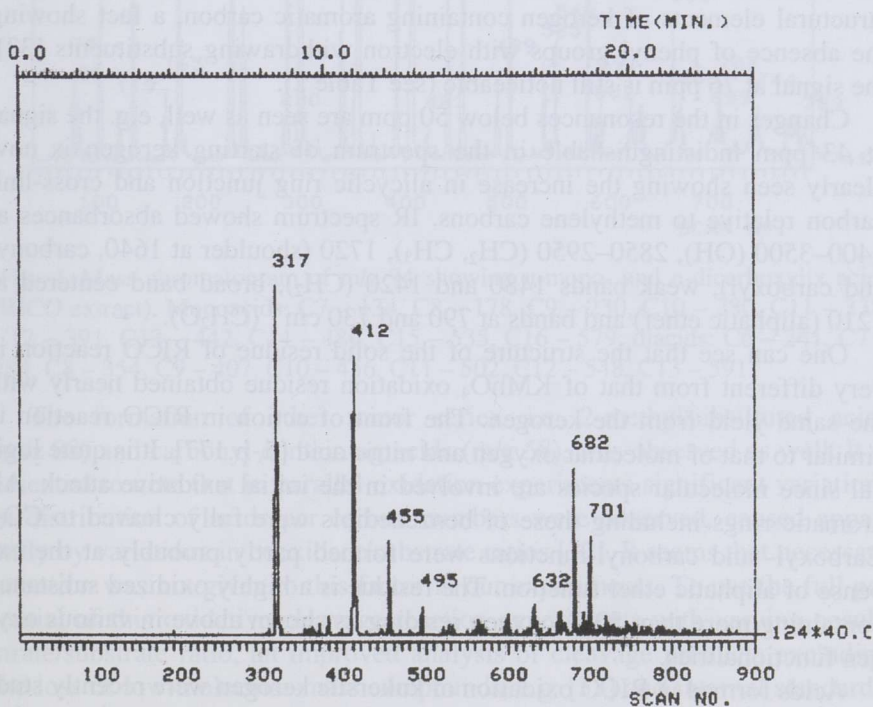


Fig. 3. Mass chromatogram of m/z 124 showing alkyl-1,3-benzenediols 682 and 701, other peaks cannot be ascribed to benzenediols (KMnO₄ extract)

Molecular ions of these compounds had m/z values 348 and 320, which might be ascribed to *n*-heptadecyl- and *n*-pentadecyl-1,3-benzenediols, respectively. However, their reversed elution order from unpolar GC column remains unclear. It should be a structural factor differentiating these compounds by their solubility in the nonpolar liquid phase of the GC column (the latter compound was supposed to be *n*-5-pentadecyl-1,3-benzenediol, the former is probably a branched-chain alkyl-1,3-benzenediol with two additional methyl groups). It seems that benzenediols are bound in kerogen via cross-links in alkyl chain and these compounds observed in trace quantities had escaped the oxidative cleavage. We note that phenolic hydroxyl groups react with diazomethane slower than carboxyl groups, and dimethylethers of 5-alkyl-1,3-benzenediols show main ion with m/z value 152 [30] not seen in this experiment.

Under RICO conditions selective cleavage of aromatic rings in various classes of organic compounds into CO_2 is well documented [31–33]. The same was observed in the case of phenolethers (VI) and (VII) which yielded as observable products only corresponding aliphatic alcohol and a mixture of aliphatic products not identified, respectively. Undecanal (IX) yielded undecanoic acid. The solid residue of kerogen oxidation was soluble in pyridine and in boiling 20 % KOH water solution, partially soluble in ethanol, insoluble in benzene. Its CP/MAS ^{13}C NMR spectrum showed the absence of structural elements of kerogen containing aromatic carbon, a fact showing the absence of phenyl groups with electron withdrawing substituents [32], the signal at 76 ppm is still noticeable (see Table 2).

Changes in the resonances below 50 ppm are seen as well, e.g. the signal at 43 ppm indistinguishable in the spectrum of starting kerogen is now clearly seen showing the increase in alicyclic ring junction and cross-link carbon relative to methylene carbons. IR spectrum showed absorbances at 3400–3500 (OH), 2850–2950 (CH_2 , CH_3), 1720 (shoulder at 1640, carbonyl and carboxyl), weak bands 1480 and 1420 (CH_2), broad band centered at 1210 (aliphatic ether) and bands at 790 and 730 cm^{-1} (CH_2O).

One can see that the structure of the solid residue of RICO reaction is very different from that of KMnO_4 oxidation residue obtained nearly with the same yield from the kerogen. The front of action in RICO reaction is similar to that of molecular oxygen and nitric acid [5, p.177]. It is quite logical since molecular species are involved in the initial oxidative attack. All aromatic rings including these of benzenediols were fully cleaved to CO_2 . Carboxyl- and carbonyl-functions were formed partly probably at the expense of aliphatic ether function. The residue is a highly oxidized substance containing more than 50 % oxygen residing as shown above in various oxygen functionalities.

Acids formed in RICO oxidation of kukersite kerogen were recently studied carefully [2]. Consistent with this above study in the present work, using selective m/z 74 monitoring, we identified two main series of these acids shown below (Fig. 4).

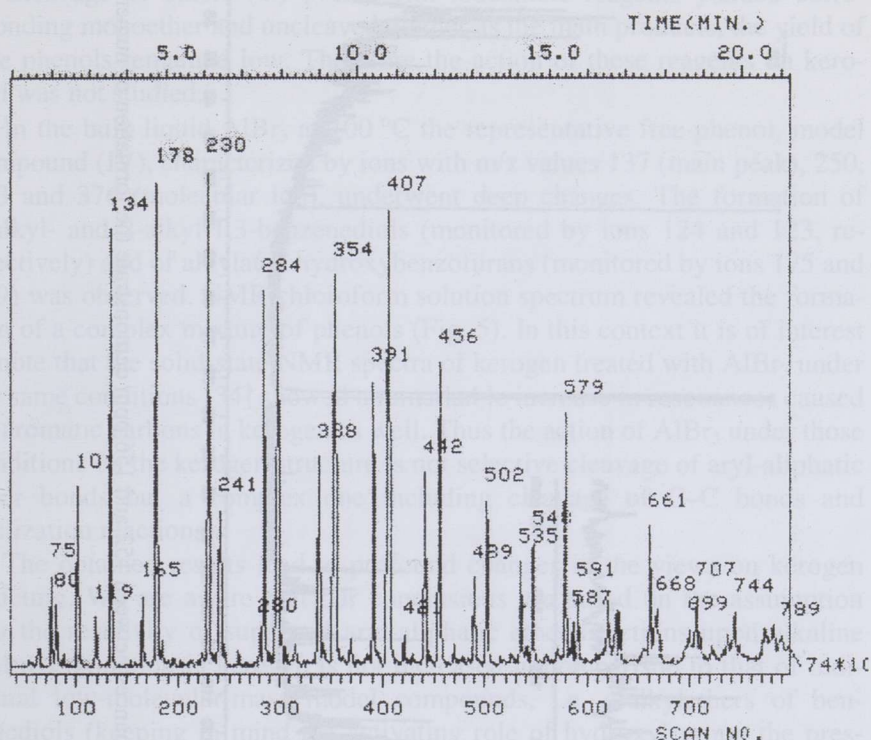
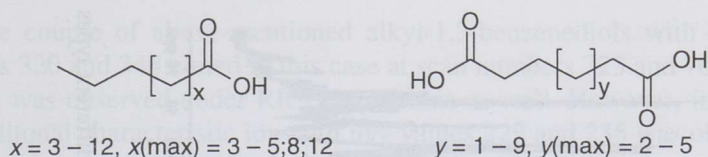


Fig. 4. Mass chromatogram of m/z 74 showing n -mono- and n -dicarboxylic acids (RICO extract). Monoacids: C7 – 134, C8 – 178, C9 – 230, C10 – 280, C11 – 338, C12 – 391, C13 – 442, C14 – 489, C15 – 535, C16 – 579; diacids: C6 – 241, C7 – 284, C8 – 354, C9 – 407, C10 – 456, C11 – 502, C12 – 548, C13 – 591

The formation of other minor series, i.e. 2-methylsubstituted acids (m/z 88) and carbonyl-containing acids (m/z 58), was observed as well. It is essential to note that in parallel oxidation experiments significant variations in distribution of acids per carbon numbers were observed, caused apparently by variations in cooxidant/substrate ratios [32]. It seems that necessary attention was not given to this factor in our experiments. To use the full potential of this oxidative cleavage reaction experiments with varying cosubstrate/substrate ratio, an improved analysis of cleavage products excluding the loss of low-molecular-mass compounds, e.g. [33] and internal standardization is necessary.

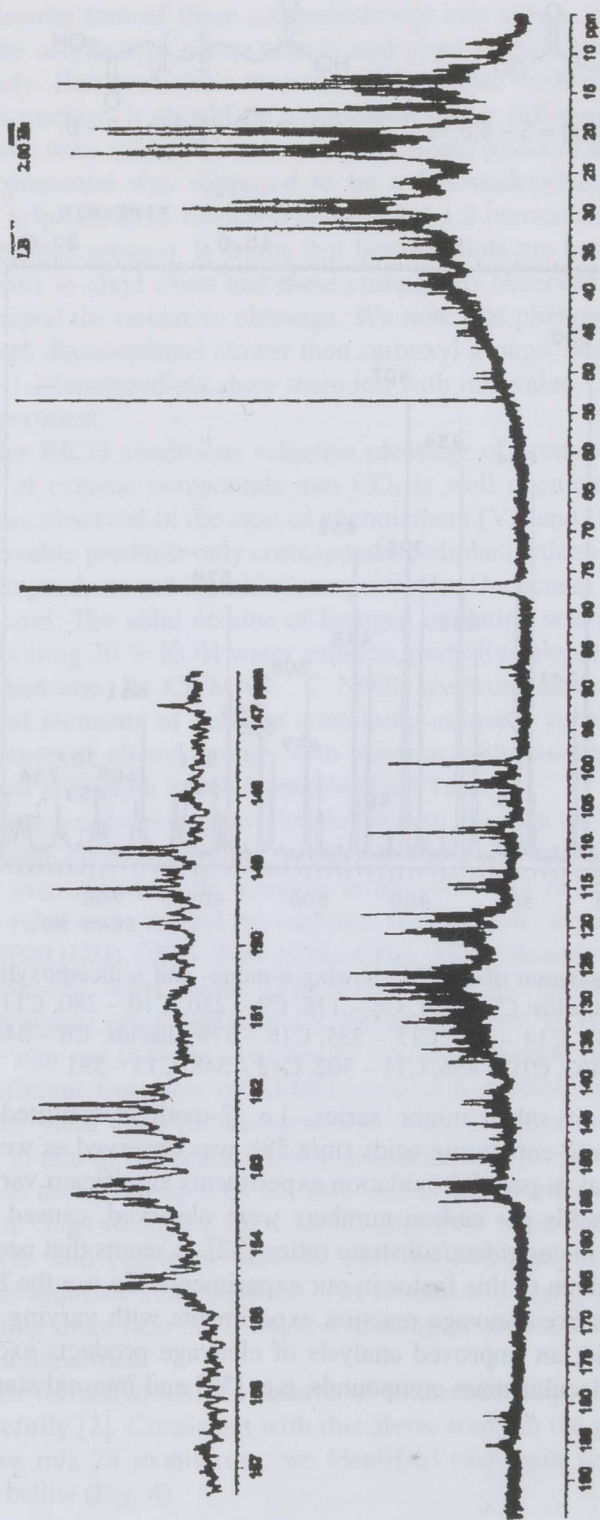


Fig. 5. ^{13}C NMR spectrum of AlBr_3 treated (IV). Resonances between 152 and 156 ppm demonstrate the formation of numerous different types of $\text{C}_{\text{air}}\text{-O}$ carbon bonds.

The couple of above-mentioned alkyl-1,3-benzenediols with molecular masses 320 and 348 eluted in this case at scan numbers 723 and 701, respectively, was observed under RICO conditions as well. However, in this case an additional characteristic ion with m/z values 222 and 235 was observed in their mass spectra, respectively.

Cleavage of ethers (V)–(VIII) with iodasilane reagents yielded corresponding monoether and uncleaved diether as the main products, the yield of free phenols remained low. Therefore the action of these reagents on kerogen was not studied.

In the bulk liquid $AlBr_3$ at 100 °C the representative free phenol, model compound (IV), characterized by ions with m/z values 137 (main peak), 250, 263 and 376 (molecular ion), underwent deep changes. The formation of 5-alkyl- and 2-alkyl-1,3-benzenediols (monitored by ions 124 and 123, respectively) and of alkylated hydroxybenzofurans (monitored by ions 175 and 189) was observed. NMR chloroform solution spectrum revealed the formation of a complex mixture of phenols (Fig. 5). In this context it is of interest to note that the solid-state NMR spectra of kerogen treated with $AlBr_3$ under the same conditions [34] showed a remarkable increase in resonances caused by aromatic carbons in kerogen as well. Thus the action of $AlBr_3$ under those conditions on the kerogen structure is not selective cleavage of aryl-aliphatic ether bonds but a complex one including cleavage of C–C bonds and cyclization reactions.

The obtained results lead to profound changes in the views on kerogen structure. We are aware that our conclusions are based on the assumption that the reactivity of supposed aryl-aliphatic ether functions upon alkaline $KMnO_4$ oxidation in kerogen is not increased in comparison to that of individual low-molecular-mass model compounds, i.e. dialkylethers of benzenediols (keeping in mind the activating role of hydroxyl group the presence of monoethers cannot be ruled out). In aquathermal reaction conditions the reactivity of this function was increased in the presence of mineral matter [35]. Such type of catalytic activity is unknown for oxidative cleavage reactions. However, certain caution is needed before making final conclusions. Further research including vacuum FTIR and action of selective reagents is necessary to get more information on the hydrogen bonds and oxygen functions of kerogen.

Conclusion

Primary and secondary dialkylethers of 1,3-benzenediols are stable under alkaline $KMnO_4$ oxidation conditions up to 95 °C. It is assumed that alkyl-1,3-benzenediols are connected to the kerogen structure via cross-links in the side chains (and possibly via aryl-aliphatic monoether bonds as well). Location of phenolic hydroxyl groups is determined by hydrogen bonds. The nature of these cross-links and hydrogen bonds needs further research.

Acknowledgements

The authors from the Institute of Chemistry are grateful to Dr. O. Parve for the possibility of cooperation with target financed theme 0350315s98, to The Estonian Science Foundation for financial support (Grant No. 4182), to ing. V. Ahelik for the preparation of kerogen sample and to Dr. R. Jäälaid for carrying out the synthesis of model ethers and cleavage experiments.

REFERENCES

1. Lille, Ü. On the origin of 5-alkyl-1,3-benzenediols in the retort oil of Estonian kukersite // Oil Shale. 1999. Vol. 16, No. 4. P. 301–307.
2. Blokker P., van Bergen P., Pancost R. D., Collinson M. E., De Leeuw J. W., Sinninghe Damste J. S. The chemical structure of *Gloecapsomorpha prisca* microfossils: Implications for their origin // Geochim. Cosmochim. Acta. 2001. Vol. 65. P. 885–900.
3. Bajc S., Ambles A., Largeau C., Derenne S., Vitorovic D. Precursor biostructures in kerogen matrix revealed by oxidative degradation : oxidation of kerogen from Estonian kukersite // Org. Geochem. 2001. Vol. 32. P. 773–784.
4. Carlsen, P.H.J., Katsuki, T., Martin, V.S., Sharpless, K.B. A greatly improved procedure for ruthenium tetroxide catalyzed oxidation of organic compounds // J. Org. Chem. 1981. Vol. 46. P. 3936–3938.
5. Fomina, A.S., Pobul, L.J., Degtereva, Z.A. The Chemical Nature of Baltic Kukersite Oil Shale and Its Properties as a Chemical Raw Material. – Tallinn : Academy of Sciences of the Estonian SSR, 1965 [in Russian].
6. Olah, G.A., Narang, S.C., Gupta, B.G., Malhotra, R. Synthetic methods and reactions. 62. Transformations with chlorotrimethylsilane/sodium iodide, a convenient *in situ* iodotrimethylsilane reagent // J. Org. Chem. 1979. Vol. 44. P. 1247–1251.
7. Lille, Ü., Bitter, L., Peinar, U. Synthesis of 2-alkylresorcinols and their infrared spectra // Proc. Estonian Acad. Sci. Chem. 1969. Vol. 18, No. 4. P. 365–369.
8. Lille, Ü.E., Bitter, L.A., Kundel, H.A. Method for the synthesis of 2-alkyl, 5-alkyl- and 2,5-alkylresorcinols // Trudy NIISlantsev. Himiya i tekhnologiya goryuchikh slantsev (Transact. of Oil Shale Research Institute. Chemistry and Technology of Oil shales). Tallinn : Valgus, 1973. No. 19. P. 121–128 [in Russian].
9. Clark-Lewis, J.W. Preparation of floroglucinol trimethyl ether // Austr. J. Chem. 1957. Vol. 10. P. 505–506.
10. Jursic, P. Synthetic application of micellar catalysis. Williamsons synthesis of ethers // Tetrahedron. 1988. Vol. 44. P. 6677–6680.
11. Mann, A.L., Patience, R.L., Poplett, I.J. Determination of molecular structure of kerogens using ^{13}C NMR spectroscopy: 1. The effects of variations in kerogen type // Geochim. Cosmochim. Acta. 1991. Vol. 55. P. 2259–2268.
12. Trewhella, M.J., Poplett, I.J.F., Grint, A. Structure of Green River oil shale kerogen. Determination using solid-state ^{13}C n.m.r. spectroscopy // Fuel. 1986. Vol. 65, Iss. 541. P. 546.

13. *Opella, S.J., Frey, M.H.* Selection of non-protonated carbon resonances in solid-state nuclear magnetic resonance // *J. Am. Chem. Soc.* 1979. Vol. 101. P. 5854–5856.
14. *Guo Shaohui.* Structural characterization of Maoming oil shale kerogen // *Oil Shale.* 2000. Vol. 17, No. 1. P. 17–23.
15. *Bhatt, M.V., El-Morey, S.S.* Silicon tetrachloride/sodium iodide as a convenient and highly regioselective ether cleaving reagent // *Synthesis.* 1982. P. 1048–1050.
16. *Ohtsuka Y., Nozawa T., Tomita A., Tamai Y., Hatano M.* Application of high-field, high-resolution ^{13}C CP/MAS n.m.r. spectroscopy to the structural analysis of Yallourn coal // *Fuel.* 1984. Vol. 63. P. 1363–1366.
17. *Derenne S., Largeau C., Casadevall E., Sinninghe Damste J. S., Tegelaar E. W., deLeeuw J. W.* Characterization of Estonian Kukersite by spectroscopy and pyrolysis : Evidence for abundant alkyl phenolic moieties in an Ordovician, marine type III kerogen // *Org. Geochem.* 1990. Vol. 16. P. 873–888.
18. *Klesment, I., Nappa, L.* Investigation of the structure of Estonian oil shale kukersite by conversion in aqueous suspension // *Fuel.* 1980. Vol. 59. P. 117–122.
19. *Largeau, C., Derenne, S., Casadevall, E., Kadouri, A., Sellier, N.* Pyrolysis of immature torbanite and of the biopolymer (PRB A) isolated from extant alga *Botryococcus braunii*. Mechanism of formation and structure of torbanite // *Org. Geochem.* 1986. Vol. 10. P. 1023–1032.
20. *Chen, C., Gao, J., Yan, Y.* Observation of the type of hydrogen bonds in coal by FTIR // *Energy & Fuels.* 1998. Vol. 12. P. 446–449.
21. *Aarna, A.J., Urov, K.* Study of the hydroxylic groups in the kerogen of kukersite oil shale // *Transact. Tallinn Polytech. Inst. Tallinn,* 1965. P. 33–42 [in Russian].
22. *Aarna, A. J., Alev, M.O.* The i.r. study of the low temperature destruction of oil shale kukersite, // *Transact. Tallinn Polytech. Inst. Ser. A, No. 210.* Tallinn, 1964. P. 3–14 [in Russian].
23. *Gubergritz, M.J.E.* Thermal Conversion of Kukersitic Oil Shale. – Tallinn, 1966 [in Russian].
24. *Coughlin, R.W., Davoudzadeh, F.* Colliquefaction of lignin and bituminous coal // *Fuel.* 1986. Vol. 65. P. 95–106.
25. *Lille, Ü., Metsik, L., Purre, T.* On the thermolysis of alkylresorcinols in static conditions // *Transact. Tallinn Polytech. Inst. Tallinn,* 1973. P. 171–176 [in Russian].
26. *Aarna, A.J., Lippmaa, E.T.* On the cleavage of ether oxygen bonds in the kerogen of the Estonian oil shale // *Zhurnal Prikladnoi Khimii (Journal of Applied Chemistry).* 1957. Vol. 30. P. 312–315 [in Russian].
27. *Raudsepp, H.T.* On the new method of research of chemical structure of combustible fossils and on the chemical structure of the Estonian oil shale - kukersite // *Proc. Acad. Sci. USSR.* 1954. Iss. 3. P. 130–135 [in Russian].
28. *Kask, K.A.* On the bituminization of kukersitic kerogen // *Transact. Tallinn Polytech. Inst.* 1956. Vol. A-73. P. 23–40 [in Russian].
29. *Brodskij E. S., Lille Ü. E., Lukashenko I. M., Bitter L. A., Poljakova A. A.* Mass-spectral data of some alkylresorcinols // *Zhurnal Organicheskoi Khimii (Journal of Organic Chemistry).* 1970. Vol. 6. P. 2096–2098 [in Russian].
30. *Lille, Ü., Rang, S., Bitter, L.* Mass spectra of alkyl resorcinol methyl ethers // *Proc. Estonian Acad. Sci. Chem.* 1975. Vol. 24, No. 1. P. 3–9 [in Russian].

31. Stock, L.M., Tse, K. Ruthenium tetroxide catalysed oxidation of Illinois No. 6 coal and some representative hydrocarbons // *Fuel*. 1983. Vol. 62. P. 974–976.
32. Ilsley, W.H., Zingaro, R.A., Zoeller, J.H. The reactivity of ruthenium tetroxide towards aromatic and etheric functionalities in simple organic compounds // *Fuel*. 1986. Vol. 65. P. 1216–1220.
33. Strausz O. P., Mojelsky T. W., Faraji F., Lown E. M., Peng P. Additional structural details on Athabasca asphaltene and their ramifications // *Energy & Fuels*. 1999. Vol. 13. P. 207–227.
34. Maremäe, E. Investigation of the Structure and Composition of Natural Macromolecular Substances Using Solid Phase High-Resolution Power Nuclear Magnetic Resonance : Final report of ESF Grant Project No. 2914 / National Institute of Chemical and Biological Physics. Tallinn, 2000 [in Estonian].
35. Siskin, M., Brons, G., Katritzky, A.R., Murugan, R. Aqueous organic chemistry. 2. Cross-linked cyclohexyl phenyl compounds // *Energy & Fuels*. 1990. Vol. 4. P. 482–488.

Presented by J. Kann

Received February 15, 2002