

STRUCTURAL CHARACTERIZATION OF MAOMING OIL SHALE KEROGEN

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The chemical structure of Maoming oil shale kerogen is studied by ruthenium tetroxide (RuO_4) oxidation. Oxidation results suggest that Maoming oil shale kerogen is of a three-dimensional-network structure with relatively short aliphatic chains as cross-linking bridges, and heteroatoms and aromatic rings are the points of attachment in the network structure.

Introduction

Shale oil can be produced from oil shale under pyrolysis. The nature of the shale oil depends upon the shale from which it was obtained as well as upon the retorting method by which it was produced. Crude shale oil has three major potential uses: as a boiler fuel, as a refinery feedstock and as a feedstock for producing petrochemicals. Chemical and physical properties of the oil shale kerogen are important for selecting the processing technology and determining what end products will be produced.

There are many methods that have been used in the study on the chemical structure of oil shale. Oxidative procedures have been widely used now to degrade complex macromolecules, such as coal, kerogen and asphalt, to simpler molecules that are more suitable for chromatographic and spectrometric studies. Knowledge of these products and their relative abundance often provide the information concerning the original aromatic and aliphatic structures in the complex macromolecules.

Generally, peripheral aliphatic structures of aromatic fragments are oxidized to yield aromatic carboxylic acids. Few methods selectively yield

aliphatic carboxylic acids. Deno and his associates [1] developed one of these methods, but its use to elucidate the structures is limited because harsh reaction conditions cause undesirable side reactions [2]. Ruthenium tetroxide (RuO_4) offers an alternative choice for these selective oxidation methods [3]. This reagent is well-known to have a property to attack selectively sp^2 carbons and functionalized carbon atoms in organic substrates: for example, this reagent was able to convert arylalkanes, diarylalkanes, functionalized carbon atoms into corresponding monocarboxylic and dicarboxylic acids.

These oxidation products may provide us valuable information about the aliphatic structures hardly obtainable using other oxidation techniques, pyrolysis experiments, etc. Aliphatic portions of coal [4-6], kerogen [7], maceral concentrates [8] and Athabasca oil sand bitumen [9] were also analyzed using this technique.

There are many studies on the chemical structure of Maoming oil shale kerogen [10-20]. However, the aliphatic nature of Maoming oil shale kerogen is still not known clearly. The purpose of this work was to study the chemical structure of Maoming oil shale kerogen with the ruthenium tetroxide oxidation method.

Experimental

RuO_4 oxidation was carried out by using a modification of the procedure proposed by Carlsen *et al* [3]. A mixture of kerogen (100 mg), carbon tetrachloride (4 ml), acetonitrile (4 ml) and doubly distilled water (6 ml) was sonicated for 1h in order to wet the sample thoroughly before ruthenium tetroxide (20 mg) and sodium periodate (2 g) were added for oxidation. Oxidation was carried out at room temperature, magnetically stirred for 48 h.

Oxidation products were separated from the reaction mixture by extraction and the acid products in the concentrated solution were methylated using 0.35 M diazomethane in ether (10 ml) before GC and GC-MS analysis. The ether was carefully removed using a rotary evaporator at an ambient temperature.

Gas chromatography (GC) was carried out on a gas chromatograph fitted with on-column injection and flame ionization detector (FID). A 30 m HP-5 capillary column with nitrogen as the carrier gas was used and programmed from 50 to 300 °C at 3 °C/min. FID signals were acquired and processed with a 9202N Data System. Quantification was achieved by GC peak area measurement. Equal FID response factors were assumed for all compounds analyzed.

Gas chromatography - mass spectrometry (GC-MS) was performed with a temperature programmed on-column injection Varian 3400 gas chroma-

tograph linked to a SSQ-710 mass spectrometer. The GC conditions were 50 °C for 1 min, then up to 300 °C at 3 °C/min. The MS was operated in electron impact mode with ionizing 70 eV, emission current 200 μ A, ion source temperature 150 °C, scan time 1.5 s.

Results and Discussion

The elemental composition of Maoming oil shale kerogen and the oxidation results are given in Tables 1 and 2. The aliphatic acid distribution is shown in the Figure. The oxidative conversion of kerogen to liquid aliphatic and aromatic acid products is only 70.5 wt.%, because unsaturated and some oxygen-containing hydrocarbons in kerogen can evolve short-chain, water-soluble acids upon oxidation, and the majority of aromatic rings are oxidized to CO₂ by RuO₄, except where electron-withdrawing groups or confused aromatic rings are present in the kerogen.

Oxidation products comprise mainly a series of aliphatic normal monocarboxylic (C₁₀-C₂₈, 24.0 %) and α,ω -dicarboxylic (C₄-C₂₆, 62.3 %) acids. In Maoming oil shale kerogen, 27 % of total organic hydrocarbons are aromatic ones [21], but only minor aromatic acids have been detected. This suggests that aromatic structures in the kerogen are present mainly as non-confused rings without electron-withdrawing groups attached and converted to CO₂. Branched chain (2-methyl) monocarboxylic acids (C₁₁-C₁₇) appear in small quantities (5 %). The ratio of normal dicarboxylic acids to normal monocarboxylic acids is 2.6, and the ratio of total straight chain acids/branched chain acids is 17.3.

RuO₄ has oxidative specificity for aromatic rings (including heteroatomic

Table 1. Elemental Analysis of Maoming Oil Shale Kerogen

C%	H%	O%	H/C	O/C
76.50	8.56	8.16	1.39	0.08

Table 2. RuO₄ Oxidation Results of Maoming Oil Shale Kerogen (Conversion*¹ 70.5 wt.%)

Aliphatic acids* ² range, %		Benzene carboxylic acids* ²					
Monoacids	Diacids	Di-acid	Tri-acid	Tetra-acid	Penta-acid	Hexa-acid	Unk.* ³
C ₁₀ -C ₂₈ 29.0	C ₄ -C ₂₆ 62.3	U.d.* ⁴	U.d.	U.d.	2.0	3.6	3.1

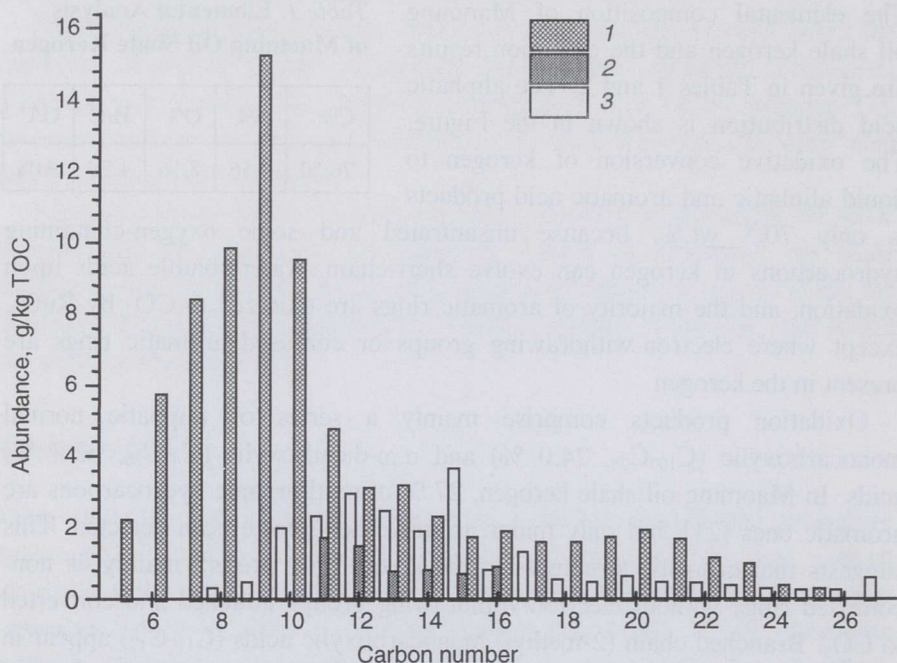
*¹ Conversion = 100(wt. sample-wt. oxidized residue)/wt. sample.

*² Percentage of total acids produced.

*³ Unk. - structurally unknown aromatic acids.

*⁴ U.d. - undetected.

varieties) and functionalized carbon atoms. Therefore, carboxylic groups often coincide with the points of attachment of alkyl fragments in the kerogen and with the positions of labile functional units, such as the proposed ether linkages in highly resistant biopolymers like 'cutan' and 'algaenan'. Aliphatic and alicyclic portions of aliphatic moieties are liberated as carboxylic acids, mainly as *n*-monocarboxylic and α,ω -dicarboxylic acids if derived from *n*-alkyl groups.



Distribution of aliphatic acids obtained from Maoming oil shale kerogen at RuO_4 oxidation: 1 – normal diacids; 2 – branched chain monoacids; 3 – normal monoacids

Dicarboxylic acids originate from bridged aliphatic chains, and monocarboxylic acids from the terminal (non-bridged) aliphatic chains. High yields of dicarboxylic acids indicate the high covalent bond cross-linking densities in the kerogen. High ratio of normal chain acids to branched chain acids indicates that normal aliphatic chains are the predominant components of the kerogen. That is in agreement with ^{13}C NMR analysis, aliphatic CH_2 is the main component (30 ppm in the spectrum) of the kerogen [21].

Aliphatic dicarboxylic acids are concentrated in relatively short chains (C_6 - C_{11}), and probably originate from an aliphatic cell-wall biopolymer derived from algae as Maoming kerogen is known to contain *Botrycoccoid* algae. According to the TEM analysis made by our group, Maoming kerogen has about 40 % ultralamellar structure. Short chain ($<\text{C}_{13}$) predominance in

dicarboxylic acids is also in agreement with the aliphatic polyaldehyde structure of *Botryococcus braunii* [22-23].

We may conclude from the oxidation results that the insoluble macromolecules in Maoming oil shale kerogen are of a three-dimensional-network structure with relatively short aliphatic chains as the cross-linking bridges. The points of the attachment in the network structure are heteroatoms and aromatic rings. Low aromaticity (0.27) [21] suggests that the chemical structure of Maoming oil shale kerogen is mainly aliphatic in nature. Aliphatic chains as the cross-linking bridges are mainly concentrated in the normal C₆-C₁₁ ranges.

Abundant solvent-soluble molecules (255.95 g/kg TOC) are present in the Maoming oil shale kerogen [24]. Soluble molecules are distributed or 'trapped' in the networks with noncovalent bond interactions between soluble and insoluble molecules. This kind of information seems to be very valuable when estimating chemical structure of oil shale kerogen and developing a more advanced utilization technology of oil shale.

Conclusions

The chemical structure of the kerogen is aliphatic in nature and the insoluble macromolecules are of a three-dimensional-network structure with relatively short aliphatic chains as the cross-linking bridges. The points of the attachment in the network structure are heteroatoms and aromatic rings. Aliphatic chains as the cross-linking bridges are mainly concentrated in the normal C₆-C₁₁ ranges. Solvent-soluble molecules are distributed or 'trapped' in the networks with noncovalent bond interactions between soluble and insoluble molecules.

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