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Structural investigations of Monterey kerogen by sequential chemical degradation

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HIGHLIGHTS

- We use successive degradation steps involving $Na_2Cr_2O_7$/AcOH and RuO_4 on kerogen.
- Tetrapyrrole pigments, occur ether- as well as sulfur-bound in the kerogen.
- A scarcely reported series of 2-methyl *n*-alkanoic acid is identified.
- RuO_4 oxidation points to the presence of aryl–alkyl ether groups in the kerogen.

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ABSTRACT

Two successive degradation steps involving $Na_2Cr_2O_7$/AcOH and RuO_4 were carried out on a Type II-S kerogen from the Miocene Monterey Formation (California) after pre-saponification of the ester bonds by KOH/MeOH treatment. Detailed gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) analysis of the soluble acids revealed significant qualitative and quantitative variation of the various types of products obtained from the two different degradation steps. Maleimides (lH-pyrrole-2,5-diones), dominated by Me,Et-maleimide, were the major degradation products released by $Na_2Cr_2O_7$/AcOH oxidation indicating that their precursors, probably tetrapyrrole pigments, occur ether- as well as sulfur-bound in the kerogen. On the other hand, a scarcely reported homologous series of 2-methyl-*n*-alkanoic acids (C_8–C_{27}) was identified as the most prominent series of carboxylic acids obtained after RuO_4 oxidation. The results support the high specificity of the RuO_4 oxidation method in revealing information on the nature of the alkyl chains substituting the aromatic moieties in the kerogen structure and point to the presence of aryl–alkyl ether groups in the kerogen. The significance of the lipid composition of the kerogen is further discussed in terms of biomarker information and their original attachment to the macromolecular structure.

1. Introduction

The most abundant form of sedimentary organic material in the geosphere consists of a macromolecular fossil organic matter termed kerogen, which if present in sufficiently high amounts will generate petroleum and natural gas under appropriate conditions. Various chemical models were proposed for the structure of kerogen ([1], and Ref. therein). Tissot and Welte [2] presented a hypothesis for the formation of kerogen, which can generally be described as the microbial breakdown of biopolymers (proteins, polysaccharides, and lignin) into biomonomers such as amino acids, simple sugars, and phenols, followed by their abiotic repolymerization or recondensation, leading to melanoidin (kerogen) formation [3]. Later, it was postulated that a significant fraction of kerogen may be derived from algal or higher plant resistant biomacromolecules, composed of polymethylenic chains with linear or isoprenoid carbon skeletons and cross-linked via ether bridges, through selective preservation [4–7].

In spite of the great progress made in the last years, the determination of the molecular kerogen structure has proven difficult due to the insolubility and the heterogeneous nature of the macromolecular organic matter. Due to the heterogeneity and the complexity of kerogen, selective chemical degradation with different reagents was employed to fragment kerogen into smaller units in order to gain insight into the types of bound lipids present and the nature of the bonds linking them to form the macromolecular matrix [8–16]. An important criterion for the usefulness of a degradation reaction is its specificity so that the molecular structures of the degradation products make it possible to draw conclusions on particular structural elements in the kerogen itself. A useful approach to unravel to some extent the structure of kerogen is the use of sequential chemical degradation, which aims at selectively cleaving different types of bonds. The reaction products then

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should allow to identify the different types of linkages of structural building blocks in the macromolecular structure [17–21].

The geochemistry of Monterey oils and their source rocks in the coastal areas of California is of considerable interest because of their unique characteristics [22]. From previous organic geochemical studies [23,24] it was concluded that the organic matter in Monterey sediments in the Santa Maria Basin is immature and derived from the remains of marine (algal) organisms deposited in a highly reducing environment. Kerogen from the Monterey Formation is commonly rich in organic sulfur (Type II-S kerogen) and believed to be the source of low-maturity oils in the California basins [25]. Previous studies by sequential selective chemical degradation of other types of sulfur-rich kerogen resulted in the recognition of specific ester-, ether- and sulfur-bound low-molecular-weight biomarkers attached to the kerogen [18,20].

In previous work [26], an account of the isolation, identification, and quantitation of carboxylic acids obtained by $Na_2Cr_2O_7$/AcOH oxidation of an immature Miocene kerogen from the Monterey Formation was reported. Quantification of the small amounts (<4.4%) of the released GC-amenable components indicated that the reagent attacked the kerogen only at the outer spheres. Further, the oxidation method did not provide any information about the sulfur-containing moieties in these sulfur-rich kerogens. Thus, a sequential selective chemical degradation study of the kerogen was initiated to provide insight into the molecular structure of the kerogen. As a first step, alkaline hydrolysis was performed in order to provide information on structural entities bound to the kerogen matrix by ester bonds, and also to reduce steric hindrance and open the kerogen matrix for consecutive degradation reactions [27]. The study resulted in the recognition of specific ester-bound biomarkers which included saturated monocarboxylic acids (C_8–C_{36}), saturated normal α,ω-dicarboxylic acids (C_7–C_{29}), isoprenoid acids (C_4–C_{17}, C_{19}–C_{21}), *iso* and *anteiso* acids (C_{11}–C_{18}), unsaturated acids ($C_{16:1}$, $C_{18:1}$), aromatic acids, hopanoic acids, 3β-carboxysteroids, as well as a complex mixture of alkylated thiophene carboxylic acids (C_1–C_6). In the present study, the structural features of Monterey kerogen were further investigated by employing two successive degradation steps of the pre-saponified kerogen concentrate.

In the first step, mild oxidation using $Na_2Cr_2O_7$/AcOH was used to cleave labile CH groups in hydrocarbon chains as well as ether and sulfur bonds. An account of the mechanism and selectivity of the oxidation was previously reported [28]. Briefly, this reagent is known to attack the CH groups at a rate determined by the hydrocarbon structure; the approximate relative oxidation rates being 1:114:7000–18.000 for methyl, methylene, and methine groups, respectively. Alkylbenzenes and polycyclic hydrocarbons containing an isolated aromatic nucleus are almost exclusively oxidized at the benzylic position. However, a drawback of the $Na_2Cr_2O_7$/AcOH degradation method is its low specificity. The reagent will also oxidize primary alcohols to aldehydes, less hindered primary alcohols to the corresponding carboxylic acids, and secondary alcohols to ketones.

In the second step, aliphatic structures of the macromolecule attached to aromatic rings were cleaved with RuO_4. RuO_4 oxidation has been previously applied for unraveling the aliphatic structure of macromolecules such as coal [29], asphaltenes [30], algaenans [6,7], and kerogen [10,13,15,21,31]. RuO_4 has oxidative specificity for aromatic units and labile functional groups such as carbon–carbon double bonds, while liberating aliphatic moieties in the form of carboxylic acids with the carboxyl-C typically representing the carbon atom in the aromatic ring to which the aliphatic chain was bound [15]. Therefore, the RuO_4 oxidation method is advantageous for elucidating the aliphatic moieties of macromolecules attached to aromatic rings.

The aim of this work is to characterize and quantify the biological markers released and provide further information about the structure and composition of Monterey kerogen.

2. Experimental

The Miocene Monterey Formation sample used in this study was supplied from the Union Science and Technology Division, Brea, CA. This sample, rich in carbon and sulfur, was taken at 1350 m depth in the Santa Maria Basin (Leroy 51–18 well). The original kerogen concentrate contained 58.3 wt% C, 6.20 wt% H, 2.67 wt% N, 12.7 wt% S, 13.4 wt% O, and 6.16 wt% ash. The values of the atomic H/C ratio: 1.28, atomic O/C ratio: 0.17, and atomic S/C ratio: 0.08 correspond to a type II-S kerogen. Methods for extraction, preparation of the kerogen concentrates, and the procedure for the alkaline hydrolysis step were reported previously [27].

2.1. Materials

All solvents were either distilled-in-glass grade or spectroscopic grade. All chemicals were reagent grade. Water was penta-distilled in an all-glass apparatus.

2.2. Sodium dichromate/glacial acetic acid oxidation

A 614 mg portion of the saponified kerogen concentrate was oxidized by stirring with a solution of 0.48 g $Na_2Cr_2O_7$ in 12 ml glacial acetic acid at 20 °C under nitrogen for 40 h. Subsequently, the mixture was filtered followed by successive ultrasonic extraction of the precipitate with distilled water (2 × 60 ml), CH_3OH (20 ml), and CH_2Cl_2 (2 × 50 ml). The filtrate and the extracts were combined, acidified with cold concentrated HCl to pH 1 and extracted with CH_2Cl_2 (2 × 50 ml). The combined CH_2Cl_2 extracts were washed with distilled water and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the residue weighed.

2.3. Ruthenium tetroxide oxidation

The RuO_4 oxidation was performed by using a modification of the procedure of Boucher et al. [10]. The residue of the kerogen sample after $Na_2Cr_2O_7$/AcOH oxidation (ca. 400 mg) was added to a suspension of sodium periodate (2 g) and ruthenium chloride trihydrate (200 mg) in a mixture of carbon tetrachloride (4 ml), acetonitrile (4 ml) and water (8 ml). The reaction mixture was sonicated for 1 h and stirred at room temperature (22 °C) for 24 h. The mixture was filtered, followed by successive ultrasonic extraction of the solid residue with distilled water (2 × 10 ml), CH_3OH (10 ml), and CH_2C1_2 (2 × 10 ml). The filtrate and the extracts were combined, acidified with 6 M HCl to pH 1 and extracted with CH_2C1_2 (3 × 20 ml). The combined organic extracts were washed with distilled water and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the residue of organic extracts weighed.

2.4. Derivatization

Carboxylic acids were esterified with diazomethane in diethyl ether before analysis as methyl esters by capillary column gas chromatography/flame ionization detector (GC/FID) and combined gas chromatography/mass spectrometry (GC/MS).