7.1 Room temperature alkaline permanganate oxidation of kerogens

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Alkaline permanganate oxidation has been used extensively in structural studies of kerogens (Vitorovic et al., 1984, 1988). However, the degradation products might not be representative "building blocks" of the macromolecular structure since alkaline permanganate would affect dramatically the chemical nature of the compounds released, thus leading to biased structural information (Maximov et al., 1977; Hatcher et al., 1981). There is, therefore, a trend towards the use of milder oxidative reagents, such as the Ruthenium tetroxide (Standen et al., 1991). In this context, we have performed a comparative study on the composition of the mixture of degradation products from a kerogen isolated from a Spanish oil shale, obtained by alkaline permanganate oxidation at room temperature and by a traditional degradation procedure at 90°C.

MATERIAL AND METHODS
The oil shale was taken from the Puertollano deposit (Stephanian B). Its geological characteristics are described in Wagner (1985). The kerogen fraction was isolated and demineralized according to standard procedures (Vitorovic et al., 1984, 1988; Standen et al., 1991). The alkaline permanganate oxidation was carried out in a flask on a heater/magnetic stirrer: 200 mg of kerogen were suspended in 5 ml of KOH 1% and 10-15 ml of KMnO₄ were added at a rate of 0.1 ml/min. Oxidations were performed at 20°C and at 90°C. Residual KMnO₄ was reduced with Na₂S₂O₅. The digests were extracted with ethyl acetate in a separation funnel, the organic phase was dried with anhydrous Na₂SO₄ and filtered, evaporated and finally methylated with diazomethane. The samples were injected on a Hewlett-Packard 5890 (FID chromatograms) and a Hewlett-Packard 5988A GC/MS system for the mass spectrometric identification of the compounds. The conditions for the GC and the GC/MS studies have been described before (Almendros et al., 1989).

RESULTS AND DISCUSSION
Fig.1 shows the Total Ion Chromatograms (TIC) of the degradation products obtained after alkaline permanganate oxidation of the oil shale kerogen at 20°C and 90°C. The identities of the compounds are indicated on each chromatographic peak. The main oxidation products in both cases were the α,ω-alkanedioic acids. When the kerogen was oxidised at room temperature, most of the products obtained were aliphatic. The sum of fat-
acids and alkanolic α,ω-diacids amounted to about 75% of the ethyl acetate-soluble, volatile degradation products, while the rest corresponded to benzenecarboxylic acids. At 90°C however, the benzenecarboxylic acids were a major group of the degradation products. This result suggests that the aliphatic components are held loosely or by low-energy bonds in the polymeric structure, whereas the aromatic moieties require comparatively more energy for release from the macromolecular network. The aliphatic components are interpreted as being derived from relatively oxidation-sensitive molecular structures, whereas the aromatic moieties would be more permanganate-resistant, the relative amounts of which tend to increase as a concomitant effect of the destruction of the former. Therefore, at room temperature there is a selective removal of the less-firmly associated aliphatic moieties. The same results have been obtained by room temperature alkaline permanganate oxidation of humic acids (Almendros et al., 1989).

A striking feature observed after room temperature alkaline permanganate oxidation is the identification of the unsaturated C_{16} and C_{18} fatty acids as degradation products. These unsaturated moieties may have been incorporated and preserved in the kerogen in an oxidation-sensitive chemical derivative and could not have been previously detected in kerogens since the methods used have been very drastic or not appropriate.

At room temperature, the released fatty acids have an even over odd predominance, with maxima at C_{16} and C_{18}, probably reflecting the original chain length distribution in the kerogen structure. The fatty acid distribution after oxidation at 90°C is very different. The proportion of short-chain alkanolic diacids increases as result of oxidation and breakdown of longer chains.

Another important difference between low and high temperature digestion is the identification of high proportions of methyl-substituted benzenecarboxylic acids after room temperature oxidation which are absent in the digests after oxidation at 90°C. The methyl-side chains are oxidized at these drastic conditions. Besides the differences in response factors between the various compound classes in the MS, there is a big difference in the benzenecarboxylic acid distribution produced at 20°C and 90°C. At 20°C there is a predominance of dicarboxylic acid isomers over the tri- and tetracarboxylic ones. At 90°C there is a predominance of the benzencarboxylic acids and a high yield of benzenetri- and benzenepenta-carboxylic acids. The latest ones need comparatively more energy for release from the macromolecular structure than the former ones.
Figure 1. Total Ion Chromatogram of the alkaline permanganate degradative products (as methyl esters) obtained at 20°C and 90°C. n: alkanedioic acids; n: alkanoic acids; φ-(COOMe)₃: benzencarboxylic acids; Me-φ(COOMe)₃: methyl benzenecarboxylic acids.
REFERENCES


7.2 Geochemical controls on the distributions of pyrrolic nitrogen compounds in crude oils

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INTRODUCTION

Nitrogen heteroatom compounds in crude oils represent one of the most important, yet poorly investigated, compound classes, and play a significant role in controlling critical Darcy Law parameters such as petroleum viscosity, interfacial tension and system wettability. Pyrrolic nitrogen species in particular constitute three quarters of total nitrogen compounds present in most oils (Snyder, 1965) and are capable of interactions with formation water and mineral surfaces via hydrogen bonding between pyrrolic N-H hydrogen and hydroxy group elsewhere, and are therefore deserving special attention. Detailed analysis of these compounds is rarely applied in petroleum geochemical studies largely due to the lack of simple and rapid techniques isolating them because of their generally low abundance in crude oils (Dorban et al., 1984; Frolov et al., 1989).

Having succeeded in isolating undistorted pyrrolic nitrogen fraction using a variety of analytical methods, we report here pyrrolic nitrogen distributions, chiefly alkylated carbazoles, benzocarbazoles and dibenzocarbazoles, determined for a wide range of crude oils and source rock extracts as part of a wider study on the origin, geochemical cycles and significance of nitrogen compounds in petroleum reservoirs.
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