

INVESTIGATION OF THE STRUCTURE OF KEROGENS BASED
ON THE OXIDATION PRODUCTS FROM MULTISTEP ALKALINE
PERMANGANATE DEGRADATION

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ABSTRACT

The stepwise alkaline KMnO_4 oxidation of Huangxian and Maoming oil shale kerogen concentrates was carried out. The oxidation products were separated with solvents and analyzed by IR, GC and GC/MS. The structure of kerogens and their behavior during oxidation have been interpreted.

INTRODUCTION

Kerogen, the most abundant organic matter in the earth's crust, is the major organic substance present in oil shale and other sediment rocks. Hence investigation on its chemical composition and structure is of theoretical values in organic geochemistry, also, of practical significance in processing of oil shale and exploration of petroleum.

Various techniques, especially the chemical degradation method^[1], have been used for investigation the structure of kerogen. In this paper, the kerogens of Huang Xian (KH) and Maoming (KM) oil shale have been studied in detail by stepwise oxidation with alkaline KMnO_4 . Referred to the works of D.Vitorovic et al.^[2-4], improvement was made on separation and analysis methods of the oxidation products. The oxidation products were extracted with ethyl ether, and then with acetone. The soluble portions were analyzed by GC and GC/MS. Also the elemental and IR analysis of each fraction of oxidation products were determined. The results obtained could be used

to interpret the oxidation behavior.

EXPERIMENTAL

1. Preparation of Samples

Huang Xian and Maoming oil shales were treated with HCL and HF for demineralizing and then extracted with a benzene-ethanol mixture for deasphalting. The chemical composition and microscopic constituents of the two kerogens are shown in Table 1.

2. Oxidation of the Kerogens

20 grams of the kerogen concentrates were oxidized in 16 steps and 15 steps for KH and KM respectively. The oxidizing degradation was carried out with 4 g KMnO_4 in 400 ml 1% KOH solution per step.

Table 1. Chemical And Microscopic Compositions of Kerogens

Sample	Chemical Composition (d, a, f)						H/C	O/C	Microscopic Constituents				
	Ash	C	H	N	O	Sorg			Sapro- pelin.	Exin. rin.	Vit- tin.	Iner- tin.	Ro%
KH	4.57	72.9	8.28	1.90	11.52	0.81	1.36	0.12	86.2	12.9	1.0	0.37	
KM	3.20	75.2	8.21	2.38	10.08	0.92	1.31	0.10	97.6	0.7	0.7	1.0	0.36

3. Separation and analysis of the oxidation products

The oxidation products were collected into two fractions fr.1, 2. For Huang Xian the products of step 1-6 was combined into fr.1 and the fr.2 was from those of step 7-16, similarly, for Maoming, the fr.1 was from step 1-5, and the fr.2 from step 5-15. The separation scheme was shown in Fig.1. The IR spectra analyses of the samples were performed quantitatively with KBr in Hitachi Model 260-50 infrared spectrometer.

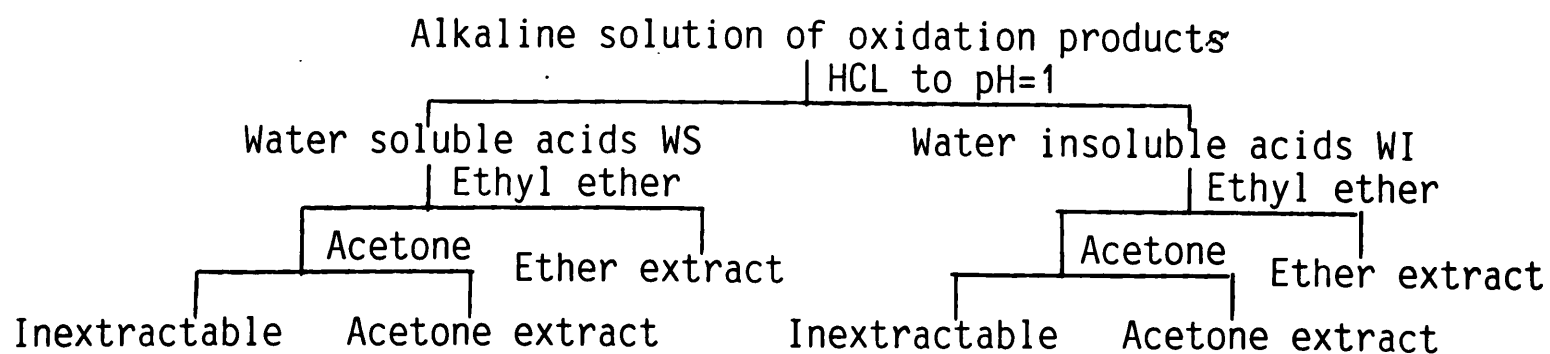


Fig. 1 Separation Scheme of Oxidation Products

The ether and acetone soluble acids were esterified with diazomethane and then analyzed by GC and identified by GC/MS. The GC were performed in a Varian Model 3400 gas chromatograph, using a fused silica capillary column (25000x0.25 mm. containing OV-101) and FID. The temperature of the column was programmed from 70°C to 300°C at 6°C/min. The GC/MS analyses were performed with a Varian Model 3700 coupled to a Varian Mat. Model 212 using a Dexil-400 fused silica capillary column. (Fig. 2 and Fig. 3)

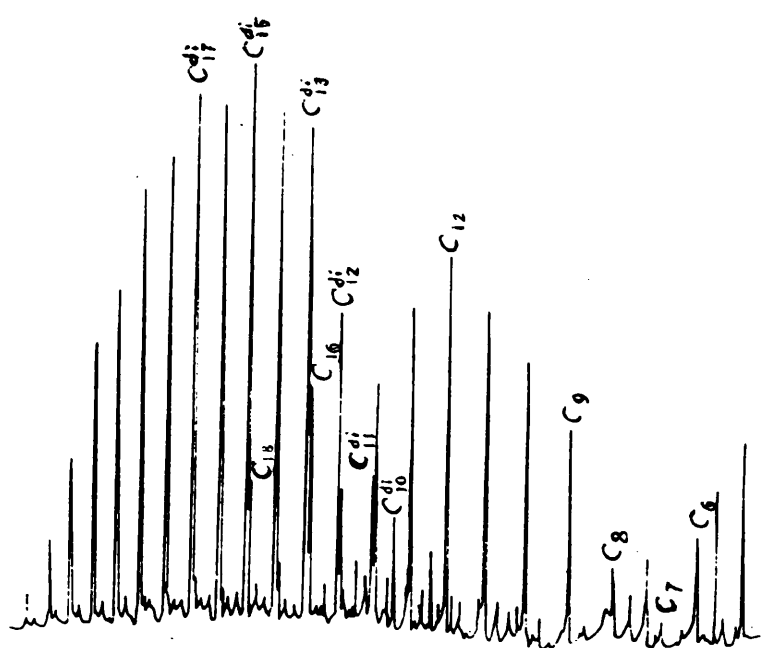


Fig. 2 Gas chromatogram of ether extract of WI fr1, in the form of methyl esters, obtained by oxidation of KH

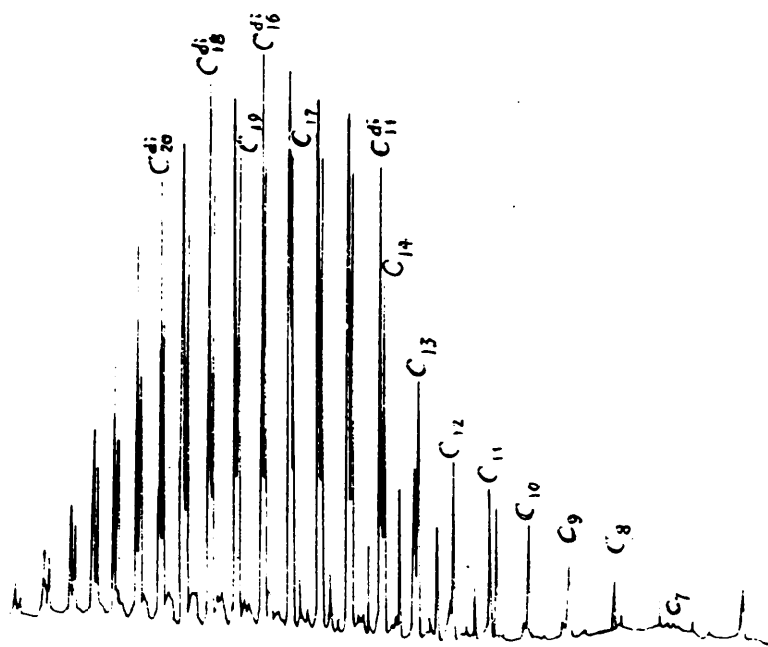


Fig. 3 Gas chromatogram of ether extract of WI fr2, in the form of methyl esters, obtained by oxidation of KH

RESULTS AND DISCUSSIONS

1. Distributions of C, N and S in the fractions of oxidation products and their effects on oxidation.

It is shown in Table 2 that the oxidation conversion for KH and KM reached 82.45% and 82.24% (based on the original carbon). Water-insoluble acid (WI) were the main oxidation products. Changes in H/C, N/C and S/C ratios of the products in Table 2, 3 show that the H/C ratio was less and N/C, S/C ratios were larger in the fr.1 than in the fr.2. It indicates that heteroatomic functional groups, bridges and aromatic structures in the kerogens were easily oxidized and concentrated in the fr.1 of the oxidation products, while the aliphatic structures were less easily oxidized and the

oxidation products concentrated in the fr. 2, predominately in the WI-fr. 2. The H/C ratio in the residues of the two kerogens were larger than that in the original kerogen, indicating that the aliphatic structures of the kerogen were more difficult to be oxidized also. The H/C ratio of WI-fr. 1 was the lowest in all the oxidation products, it shows that the macromolecular aromatic compounds were concentrated in it. Moreover, the H/C ratio of this fraction in KH was obviously lower than that in KM, which was contrary to H/C ratios of the original kerogens, implying that the nature of the aromatic structures in two kerogens was different.

Table 2. Atomic Ratios of the Kerogens and their Oxidation Products

Sample		Kero- gen	Resi- due	Vola- tile Acids	C lost inco	Watersolu- ble acids (WS)		Waterinsol- uble acids (WI)		C yield of acids
						1	2	1	2	
						KH	H/C	1.36	1.52	
	N/C	0.022	0.007			0.15	0.036	0.04	0.015	
	S/C	0.004								
	C	100	1.18	1.19	16.37	7.4	16.5	13.14	44.21	82.45
KM	H/C	1.31	1.64			1.48	1.27	1.17	1.69	
	N/C	0.027	0.008			0.133	0.042	0.043	0.016	
	S/C	0.005								
	C	100	1.17	1.71	16.59	7.4	12.43	15.76	44.96	82.24

Table 3. Atomic Ratios of Solvent Soluble Acids

Sample		Extracts of WS with solvents				Extracts of WI with solvents			
		ether		acetone		ether		acetone	
		1	2	1	2	1	2	1	2
KH	H/C	1.47	1.58	1.31	1.41	1.68	1.78	1.18	1.67
	N/C	0.012	0.005	0.042	0.021	0.005	0.006	0.025	0.013
	S/C	0.018	0.002	0.016	0.006		0.002	0.006	0.004
	C %	4.76		7.11		18.50		17.95	
KM	H/C	1.65	1.76	1.29	1.49	1.45	1.73	1.11	1.62
	N/C	0.018	0.008	0.049	0.024	0.012	0.007	0.34	0.016
	S/C	0.007	0.003	0.015			0.004	0.009	0.004
	C %	4.19		5.84		19.26		13.36	

In the acids obtained, 48.32% and 42.65% may be extracted by organic solvents with respect to the carbon content of KH and KM. The H/C ratios of the acetone soluble acids were less, but N/C and S/C ratios were higher

than those of the ether soluble acids, indicating that there were more aromatic and heteroatomic compounds in the acetone extract.

The nitrogen and sulfur compounds in the kerogens were very readily oxidized, their oxidation products were concentrated in water-soluble acids (WS) with low molecular weight.

2. Interpretation of the chemical structure of kerogens and its behavior in oxidation by IR spectrometric analysis.

It was shown in Table 4 that the absorption intensity ratios representing the relative amount of aromatic and aliphatic structures, and the absorption intensity ratios related to the oxygen containing functional groups both were larger in the fr. 1 than in the fr. 2 and corresponding kerogen. The band intensity ratios representing the relative quantities of long-chain methylene were larger in the fr. 2 than those in the fr. 1 and corresponding kerogen as well. This may indicate that the aromatic nuclei attached with more oxygen containing functional groups were degraded by oxidation prior to the aliphatic structures in the kerogen. The aromatic acid with low molecular weight, was extracted into the water-soluble products, and most of them present in the WI-fr. 1 as macromolecules with multifunctional groups. However, the aliphatic structures especially with long-chain were more difficult to be oxidized than the aromatic nuclei. After oxidation, most of the aliphatics were present in the WI fr.2 in the form of aliphatic carboxylic acids. It is found in Table 4 that more aliphatic carbons, especially the long chain aliphatic carbons, were remained in the residues, confirming that the aliphatic structures were more difficult to be oxidized.

Tab. 4 Relative IR Absorption Intensities of the Two Kerogens and Their Oxidation Products

Sample	Aromatics		CH ₃	CH ₃	(CH ₂) _{n≥4}	(CH ₂) _{n≥4}	bands related to oxygen functional group			AromC-H
	Aliphatics		CH ₂	CH ₂ +CH ₃	CH ₂	CH ₂ +CH ₃				AromC=C
	D1620	D1620	D1380	D1380	D720	D720	D1710	D1410	D950	D870
	D2920	D1460	D2920	D1460	D2920	D1460	D2920	D2920	D1710	D1620
KH:	0.211	1.011	0.030	0.190	0.048	0.229	0.259			0.045
WI-fr1	1.624	2.832	0.716	1.248			2.467	0.670	0.333	
WI-fr2	0.190	0.492	0.209	0.542	0.108	0.282	0.938	0.271	0.321	
Residue	0.130	0.738	0.063		0.050	0.357	0.483			
KM:	0.279	1.327	0.065	0.310	0.046	0.220	0.290			0.010
WI-fr1	1.303	2.680	0.574	1.118	0.032	0.066	2.060	0.506	0.265	
WI-fr2	0.197	0.704	0.177	0.633	0.063	0.225	0.754	0.192	0.412	
Residue	0.148	0.701	0.082	0.388	0.063	0.239	0.489			

According to the IR analyses of the two kerogens and their oxidation products (See Table 4), it is obvious that the aliphatic long-chain structures predominate in the two kerogen matrices. Comparing KH with KM, there were more aliphatic structures especially long chains, and slightly less aromatic nuclei in the former. It should be mentioned that according to D870/D1620 the aromatic system of KH was more compact than that of KM. The macromolecular aromatics in the oxidation products of KH were mainly in the WI-fr. 1. The methyl group in aliphatic structure of KM was found higher than that of KH. The fact that 950 cm absorption band was quite strong in the IR spectra of the WI-fr. 2 of KM is not only due to the oxygen containing functional groups but also the alicyclic structures.

The IR analyses testified that the nitrogen groups in the kerogens were easily oxidized and largely into the water soluble acids, confirming to the results of elemental determination. The existence of the absorption bands representing carbonyl group of amides and aliphatic cyanides in the IR spectra of the WS may indicate that not all nitrogen atoms were present in the heteroaromatic ring system of the kerogen.

3. GC and GC/MS analyses of the solvent soluble acids of the oxidation products.

The ether and acetone extracts obtained from the WS and WI were esterified with diazomethane, and the esters were analyzed by use of GC and GC/MS. The results indicated that the unbranched aliphatic C_2-C_{30} dicarboxylic and C_7-C_{31} monocarboxylic acids were the major components in every fraction of the extracts, except the acetone extract of WI-fr. 1. In particular, the long-chain aliphatic mono- and dicarboxylic acids predominated in the chromatogram of the ether extracts.

From the chromatogram of ether extract of the WI, it is found that the content of saturated long-chain monocarboxylic acids increased in the later oxidation stage. Based on the information from GC, IR, and elemental analyses, the kerogen matrices of Huang Xian and Maoming shale may be thought as three-dimensional macromolecular stereo-network structures consisting of aliphatic clusters and aromatic fragments interconnected by long polymethylene and/or heteroatomic bridges. The aromatic nuclei, heteroatomic groups and bridges were oxidized easily and resulted in formation of unbranched monocarboxylic and/or dicarboxylic acids with low mo-

molecular weight by cleavage at connecting point of side chains or bridges, and then the aliphatic clusters were oxidized at the methylene bridge or saturated side chain to form long-chain di-and/or monocarboxylic acids. Meanwhile, the saturated long-chain monocarboxylic acids entrapped originally in the clusters^[5] were set free, so as to increase the amount of the long-chain monocarboxylic acids.

It was found that the ratio of the unbranched aliphatic monocarboxylic acids to dicarboxylic acids increased as the H/C ratio of the kerogen decreased.

The analyses results of the solvent extracts from the WS indicated that the aliphatic unbranched dicarboxylic acids with low molecular weight were the main constituents, and there was considerable amount of aromatic carboxylic acid and heteroatomic compounds in the fr. 1. The aromatic polycarboxylic acids were mostly extracted in acetone. For KM the aromatic carboxylic acids consist mainly of o-phthalic acid and benzene tricarboxylic acid, moreover, significant amount of benzoic acid was found also. These all indicate that the aromatic nuclei were mostly kata-condensed and less compact in KM matrix. On the other hand, no significant quantity of benzoic acid has been found in Huang Xian WS. The acetone extracts of WS-fr. 1 was identified by use of GC/MS, results show that they consist of benzene di-, tri-, tetra-, penta- and hexa- carboxylic acids as well as small amount of aromatic carboxylic acids with methyl and methoxy group, being abundant in benzene tetracarboxylic acid and then the benzene tricarboxylic acid and o-phthalic acid. This further indicated that the aromatic nuclei in KH were more condensed than in KM, and the kata-condensed rings existed in considerable proportion. Results from GC analyses testified that there were more long-chain aliphatic structures in KH than in KM, however more methyl-branched aliphatic and naphthenic structures were present in the later.

CONCLUSIONS

1. The elemental analyses indicated that H/C and O/C ratios of KH were larger than those of KM, while the N/C and S/C of KH were less than those of KM. Both KH and KM belong to type II^[6] The reflectance of vitrini-

tes (Ro) showed that maturity of two kerogens was very near, so that they may be comparable in the chemical composition and structure.

2. Studies in the chemical structures of KH and KM were performed by stepwise oxidation with alkaline KMnO_4 . The oxidation conversion for KH and KM reached to 82.45% and 82.24% (based on organic carbon), so more accurate information about the structure of kerogens could be obtained.

3. From elemental analyses and IR measurements of the kerogens, oxidation products and residues it was found that the heteroatomic groups, bridges and aromatic nuclei in the kerogen matrices were first attacked by oxygen, resulting in the formation of aromatics and heteroatomic compounds considerably concentrated in the fr. 1 of the oxidation products, and the aliphatics, especially with long chain, remained in quite large amounts in the residues.

4. The ether and acetone extracts (yields 48.32% and 42.65% based on organic carbon) obtained from the oxidation products were analyzed by GC and GC/MS. The results revealed that the unbranched aliphatic dicarboxylic acids ($\text{C}_2\text{-C}_{30}$) and mono carboxylic acid ($\text{C}_7\text{-C}_{31}$) were the major components. The information obtained from GC, GC/MS, IR and elemental analyses testified that aliphatic long-chains were the major structural constituents both in KH and KM.

5. The results of analyses showed that KH was slightly richer in aliphatic structure than KM, especially the aliphatic long-chain structure was much more abundant in the former. However, the proportion of methyl-substituted chain and alicyclic structures were higher in KM. It seems that KM might contain the more steroid and isoprenoid structures. The condensation degree of the aromatic nucleus in KH was higher than that in KM. Considerable part of the aromatic rings were kata-condensed in both kerogen structures.

6. The Huang Xian oil shale contains more organic matter, (38.34% and 17.04% respectively) and less heteroatoms than Maoming oil shale. The former can be more easily oxidized than the latter, their oxidation products consisting of aliphatic unbranched dicarboxylic acids predominately. Moreover, the aromatic and heteroatomic structures were first oxidized, this made the separation and purification of the oxidation products possible and convenient. Therefore, this work shows the potential for produc-

ing aliphatic long-chain dicarboxylic acids by oxidation of Huang Xian oil shale.

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