Journal of Thermal Analysis, Vol. 36 (1990) 2465-2473

THERMOANALYTICAL CHARACTERIZATION OF ALEKSINAC (YUGOSLAVIA) OIL SHALE KEROGEN

D. Vucelic[1, 3], *V. D. Krsmanovic*[1, 2], *V. Vucelic*[3], *M.Kicanovic*[3] and *D. Vitorovic*[1, 2]

DEPARTMENT OF CHEMISTRY AND PHYSICAL CHEMISTRY, FACULTY OF SCIENCE, UNIVERSITY OF BELGRADE, P. O. BOX 550, YU-11001 BELGRADE, YUGOSLAVIA[1]
INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, BELGRADE, YUGOSLAVIA[2]
INSTITUTE OF GENERAL AND PHYSICAL CHEMISTRY, BELGRADE, YUGOSLAVIA[3]

(Received April 3, 1990)

The chemical nature of the kerogen from Aleksinac (Yugoslavia) oil shale was studied by thermal analysis of a kerogen concentrate and the partially degraded kerogen concentrates obtained as intermediates in its stepwise alkaline permanganate oxidation. The initial kerogen concentrate decomposed in the range 200-550°C and the DTG profile consisted of several overlapping peaks. The partially degraded kerogen concentrates were thermally more stable. Their thermograms consisted of two distinct parts: the low- (150-420°C) and the high-temperature (420-650°C) part. Each of them was complex, involving two or more components. On the basis of IR data, it was suggested that the low-temperature part corresponded to the thermal degradation of aliphatic, and the high-temperature part to the degradation of aromatic components.

Oil shales represent an intimate mixture of organic and inorganic material. Moreover, the organic material is not homogeneous. In contrast with a small proportion of the organic material called bitumen (usually up to 5%), which is soluble in organic solvents, the main portion is the insoluble macromolecular kerogen. Before study of the kerogen by any method, it is usually necessary to remove most of the other material from the shale. However, appropriate chemical procedures are generally tedious and even the best of them do not allow the complete isolation of native kerogen. Usually, small portions of pyrite and silicates remain in the shale kerogen concentrates.

The macromolecular nature of the kerogen and consequently its insolubility have restricted the use of most instrumental methods for its struc-

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

tural investigation. Although this was not the case with TG, only a few papers relating to TG investigations of kerogens have been published so far, e.g. a review paper by Durand-Souron [1]. However, the presence of inorganic material and the heterogeneity of kerogen were shown to make the interpretation of the TG results difficult.

The best approach for studying the structure of the heterogeneous kerogen would be to start with a model organic material similar to kerogen, but more homogeneous. For this purpose, pure aromatic or aliphatic fractions of the kerogen should be advantageous. However, mechanical separation of the individual kerogen structural components is not possible. Therefore, a chemical approach for kerogen concentrate "fragmentation" was chosen, i.e. stepwise alkaline permanganate degradation, yielding as main intermediate solid oxidation products, on one hand the partially degraded kerogen concentrates and on the other hand the high molecular weight "precipitated acids", both quantitatively and structurally relevant to kerogen. On the basis of the different sensitivities of the various individual kerogen constituents towards the oxidant, as reported earlier [2, 3], chemically more homogeneous fragments, i.e. oxidation products with retained kerogen structural characteristics, were obtained. Hence, these products were considered to be convenient substrates in TG studies of kerogen. One group of these degradation products, the precipitated acids, were studied earlier [4, 5].

This work was aimed at studying the more complex substrates, i.e. the initial kerogen concentrate and the partially degraded concentrates obtained in the same stepwise alkaline permanganate degradation. The paper reports parallel thermal analyses of these substrates.

Experimental

Preparation of initial kerogen concentrate

The initial kerogen concentrate (KC-0) was prepared from a representative sample of the oil shale from Aleksinac (Yugoslavia). The shale sample was powdered to –100 mesh (Tyler) and the kerogen concentrate was prepared by successive treatment of the shale with benzene (72 h), hydrochloric acid (1:10), benzene (36 h), potassium hydroxide in methanol (24 h), concentrated hydrofluoric-hydrochloric acid (1:1), distilled water and, finally, a benzene-methanol mixture (1:1, 3x36 h). The composition [6] of the resulting kerogen concentrate KC-0 is shown in Table 1. The elemental composition of the KC-0 kerogen was 68.79% C, 6.89% H, 2.46% N and 21.86% O + S (by difference).

Table 1 The yields and the composition of the initial and partially degraded kerogen concentrates (%, relative to kerogen concentrate)

Kerogen concentrate	Yield, g	Pyrite, %	Non-pyritic mineral matter, %	Kerogen (by difference), %
KC-0	-	26.5	1.1	72.4
KC-1	2.8558	19.4	1.4	79.2
KC-3	2.5473	16.8	1.8	81.4
KC-6	2.1451	16.7	1.4	81.9
KC-12	1.2364	22.2	2.1	75.7
KC-15	0.9193	28.7	2.1	69.2

Preparation of partially degraded kerogen concentrates

Five identical 3.34 g portions of KC-O were subjected separately to stepwise alkaline permanganate degradation according to the procedure described earlier [2-5, 7]. The kerogen concentrates were dispersed in 100 cm^3 1.6% KOH and oxidized at 75° with 0.50 g portions of $KMnO_4$. After the reduction of each portion of permanganate, the alkaline solution (containing soluble degradation products) was separated by centrifugation. The solid residues were successively used (one at a time) for the isolation of the partially degraded kerogen concentrates, and the others were further oxidized with new portions of permanganate. The first sample of KC-0 was oxidized in one step (the partially degraded kerogen concentrate was denoted KC-1), the second was oxidized in three steps (KC-3), the third in six steps (KC-6), the fourth in twelve steps (KC-12) and the fifth in fifteen steps (KC-15). The partially degraded kerogen concentrates were isolated by successive treatment [3, 7] of the corresponding solid residues with 4 % oxalic acid in 0.5 M sulphuric acid (three times) and distilled water until free from oxalate. The resulting kerogen concentrates were dried at 80°. Their yields and the compositions [6] are given in Table 1. The elemental compositions of the corresponding kerogens are shown in Table 2.

Thermogravimetric analyses

Thermogravimetric analyses (20-700°) of KC-0 and the partially degraded kerogen concentrates were carried out on a DuPont 951 thermogravimetric analyser (plug-in module for the DuPont 990 thermal analyser). The ambient atmosphere was nitrogen at a flow rate of 15 cm^3/min. The size of the sample was about 5 mg and the heating rate was 5 deg/min.

Table 2 Elemental composition of the kerogen in the partially degraded kerogen concentrates

Kerogen concentrate	Elemental analysis, % C	Elemental analysis, % H	Atomic H/C ratio
KC-1	72.94	6.89	1.14
KC-3	67.61	6.82	1.20
KC-6	71.92	8.18	1.36
KC-12	68.44	8.44	1.47
KC-15	69.29	9.32	1.60

IR spectra

IR spectra of KC-0 and the partially degraded kerogen concentrates were obtained on a Carl Zeiss Specord 75. The preheated samples were prepared by heating the kerogen concentrates to 460° under nitrogen in the thermogravimetric analyser (5 deg/min). The samples were then kept for one hour at 460°, cooled and used for the preparation of KBr pellets. The IR spectra of the preheated samples were obtained on a Perkin-Elmer 457 spectrometer.

Results and discussion

The kerogen concentrate of Aleksinac (Yugoslavia) oil shale denoted KC-0 [4] was partially degraded by stepwise alkaline permanganate oxidation. The stepwise oxidation provided two related sets of solid degradation products, differing in the degree of degradation, a set of precipitated acids (from steps 1, 2-3, 4-6, 7-9, 10-12 and 13-15), which were studied earlier [4, 5], and a set of partially degraded kerogen concentrates (originating from steps 1, 3, 6, 12 and 15) for investigation in this paper.

The yields and the compositions of the partially degraded kerogen concentrates (Table 1) were used for estimation of the extent of kerogen and pyrite oxidation. During the first three degradation steps, more than 50% of the pyrite and less than 15% of the kerogen were oxidized (Fig. 1). In later steps, the oxidation of kerogen was favoured in comparison with that of pyrite.

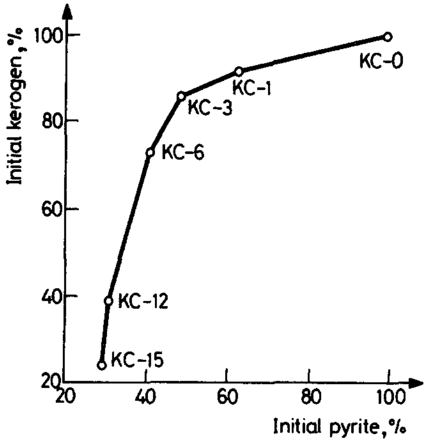

Fig. 1 Changes of the kerogen and pyrite contents during chemical degradation

It was observed that the aromatic (coaly type) portion of this kerogen was more susceptible towards alkaline permanganate, while the aliphatic material was more resistant. This finding resulted from GC-MS analysis of the methyl esters of ether-soluble acids [2] and by parallel chemical and micropetrographic analysis of both precipitated acids and partially degraded kerogen concentrates [3]. Therefore, the mentioned sets of partially degraded kerogen concentrates and the precipitated acids were expected to represent series of samples with a decreasing share of aromatic material and an increasing share of aliphatic material, and vice versa. For example, the aromatic material being more reactive towards permanganate, it was expected that the partially degraded kerogen concentrate from the first degradation step, KC-1, should contain less aromatic material than the initial kerogen concentrate, KC-0. On the other hand, the precipitated acids from the first degradation step, PA-1, should contain more aromatic material than those from the later steps, etc.

The gradual increase in the atomic H/C ratio of the kerogen from the partially degraded concentrates KC-1 to KC-15 (Table 2) indicated a loss of aromatic components and hence an increase in aliphaticity. A recent study [8] of both precipitated acids and the partially degraded kerogen concentrates by Curie point pyrolysis-GC and pyrolysis-GC-MS corroborated these findings.

The IR spectra shown in Fig. 2, in contrast with the findings on the precipitated acids [4], did not fully confirm this observation, although all partially oxidized concentrates showed lower aromatic peaks in comparison with KC-0. However, among the concentrates themselves, from KC-1 to KC-12, it was difficult to observe any substantial change in the aliphatic/aromatic ratio. The uniformity of the spectra showed that the basic kerogen structure was mainly preserved during the first stages of degradation. However, the KC-12 spectrum was quite different. The shapes of the peaks in the range 700-1700 cm^{-1} were changed. The aliphatic peaks, although present (2800-2900 cm^{-1}), had very low intensities. Finally, due to substantial oxidative degradation, KC-15 completely lost the characteristics of the kerogen IR spectra.

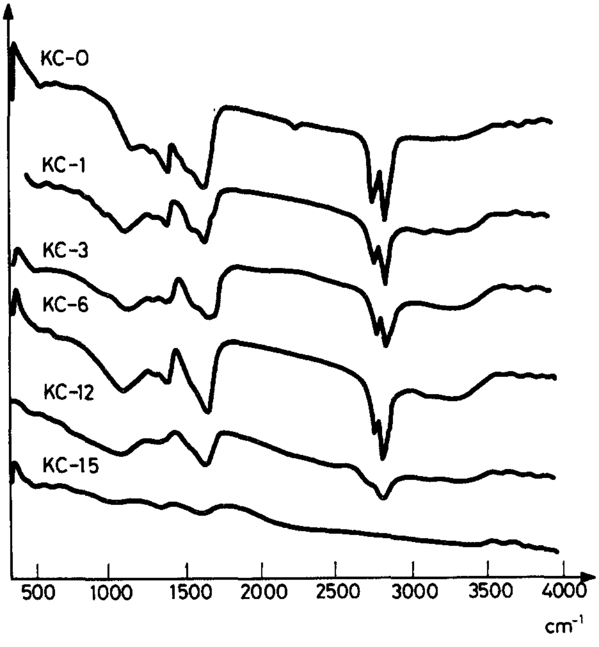

Fig. 2 IR spectra of the initial and partially degraded kerogen concentrates

By thermal analysis, the initial kerogen concentrate KC-0 decomposed in the range 200-550° and the DTG trace consisted of several highly overlapping peaks with different thermal properties (Fig. 3).

All the thermograms of partially degraded kerogen concentrates were similar (except for KC-15), but their peaks were distributed in a wider range (from 150 to 650°), indicating a lower thermal stability of the starting kerogen concentrate. The different thermal behaviour of KC-15 was probably a result of drastic chemical degradation. The thermograms of partially degraded kerogen concentrates (except for KC-15) consisted of two distinct parts: a low-temperature (150-420°) and a high-temperature (420-650°) part. Each of them was complex, consisting of two or more components. The resolution between two complex peaks was increased during chemical degradation and similar behaviour was found for precipitated acids [4, 5].

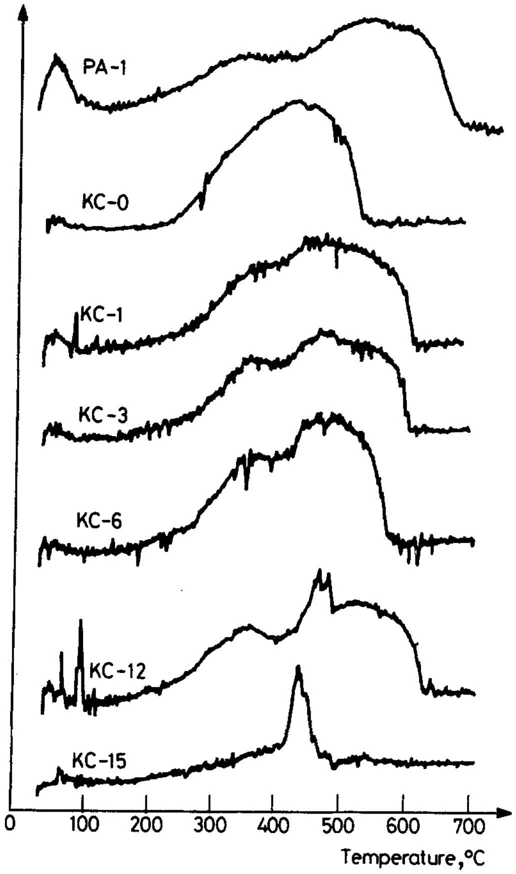

Fig. 3 DTG analysis of the precipitated acids PA-1, the initial (KC-0) and the partially degraded kerogen concentrates

The precipitated acids and the partially degraded kerogen concentrates, as oxidation products of the shale kerogen, were both thermally more stable than the original kerogen (Fig. 3).

The thermograms of the partially degraded kerogen concentrates more closely resembled those of the precipitated acids than the thermogram of the initial concentrate KC-O. However, several differences were observed:

(a) thermally, the precipitated acids were more stable [4, 5] than the precursor kerogen or its residue in the kerogen concentrates. A similar relationship was found between humic acids and their possible precursors, lignin and cellulose [9, 10].

(b) between 450 and 500°, the concentrates showed a very intensive (particularly KC-12 and KC-15) pyrite double peak. Naturally, the thermograms of the precipitated acids did not show this peak.

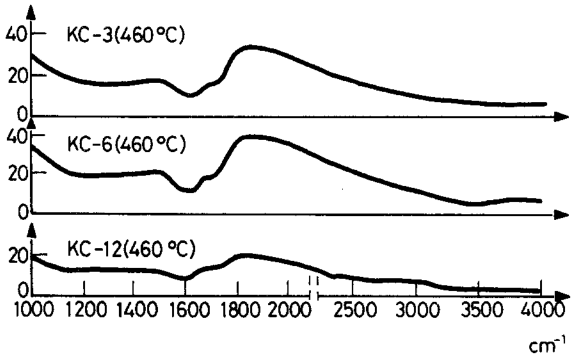

Fig. 4 IR spectra of partially degraded kerogen concentrates (after heating for one hour at 460°C)

The differences in thermal stability should be attributed to the structural differences of the organic matter. The chemical natures of the low- and high-temperature parts were studied by combining thermal and IR analyses. The samples heated in a DuPont 990 thermal analyser from 20 to 460° and then kept for one hour at 460° were analysed by IR. The IR spectra of the residues of the partially degraded concentrates (Fig. 4) contained only carbonyl (1720 cm^{-1}) and aromatic structure (1640 cm^{-1}) peaks. These results, as has been demonstrated earlier for precipitated acids [4], showed that the low-temperature part of the thermal curve related to aliphatic structures, while the high-temperature part originated from aromatics. Hence, the aliphatic compounds are more stable in oxidative degradation, but less stable in thermal degradation, quite opposite to the behaviour of aromatic structures.

Thus, the thermogravimetric method was found to be useful for characterization of the initial and the partially degraded kerogen concentrates. Nevertheless, although the thermal profiles of the partially degraded concentrates were much better resolved in comparison with the thermal profile of the kerogen precursor KC-0, because of several overlapping peaks which still remain, an exact computer PDTG analysis [5] would be necessary for a better understanding of the structural details of the substrate.

References

1 C. Durand-Souron, Kerogen, Insoluble Organic Matter from Sedimentary Rocks, Editions Technip, Paris 1980, p. 143.

2 D. Vitorovic, M. V. Djuricic and B. Ilic, Advances in Organic Geochemistry 1973, Edition Technip, Paris 1974, p. 179.

3 V. D. Krsmanovic, M. Ercegovac and D. Vitorovic, Org. Geochem., 1 (1978) 85.

4 V. D. Krsmanovic, V. Vucelic, D. Vucelic and D. Vitorovic, J. Thermal Anal., 32 (1987) 835.

5 D. Vucelic, V. D. Krsmanovic, V. Vucelic and D. Vitorovic, J. Thermal Anal., 34 (1988) 1231.

6 S. Lj. Jovanovic and D. Vitorovic, Bull. Soc. Chim. Beograd, 17 (1952) 347.

7 D. Vitorovic, V. D. Krsmanovic and P. A. Pfendt, Advances in Organic Geochemistry 1979, Pergamon Press, Oxford 1980, p. 585.

8 V. D. Krsmanovic, D. Vitorovic, E. W. Tagelaar, J. W. de Leeuw and P. A. Schenck, Proc. 8th Int. Symp. Pure Applied Pyrolisis, Lund, Sweden, June 13-17 (1988).

9 W. Naucke, 4. Torf-Kolloquium DDR-VR Polen 1/6, Rostock (1967).

10 F. Paulik and M. Weltner, Acta Chim. Acad. Sci. Hung., 16 (1958) 159.

Zusammenfassung — Mittels Thermoanalyse eines Kerogenkonzentrates und als Zwischenprodukte einer schrittweisen alkalischen Permanganatoxidation erhaltener, teilweise abgebauter Kerogenkonzentrate wurde die chemische Natur von Kerogen eines Ölschiefers aus Aleksinac (Jugoslawien) untersucht. Das ursprüngliche Kerogenkonzentrat zersetzt sich im Bereich 200-550°C, die DTG-Kurve besteht aus mehreren überlappenden Peaks. Die teilweise abgebauten Kerogenkonzentrate waren thermisch stabiler. Ihre Thermogramme gliedern sich in zwei Teile: in den Niedrig- (150-420°C) und in den Hochtemperaturbereich (420-650°C). Alle waren komplexer Natur, bestehend aus zwei oder mehr Komponenten. IR-Untersuchungen lassen darauf schließen, daß der Niedrigtemperaturbereich dem thermischen Abbau der aliphatischen, der Hochtemperaturbereich hingegen dem Abbau der aromatischen Bestandteile entspricht.