

**THERMOANALYTICAL CHARACTERIZATION OF
PRECIPITATED ACIDS OBTAINED BY ALKALINE
PERMANGANATE DEGRADATION OF THE KEROGEN
FROM ALEKSINAC (YUGOSLAVIA) OIL SHALE***

V. D. Krsmanović^{1,2}, V. Vučelic³, D. Vučelic^{1,3} and D. Vitorović^{1,2}

DEPARTMENT OF CHEMISTRY, AND PHYSICAL CHEMISTRY,
FACULTY OF SCIENCE, UNIVERSITY OF BELGRADE,
P.O. BOX 550, YU-11001 BELGRADE, YUGOSLAVIA¹
INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY,
BELGRADE, YUGOSLAVIA²
INSTITUTE OF GENERAL AND PHYSICAL CHEMISTRY, BELGRADE,
YUGOSLAVIA³

(Received June 10, 1986)

The precipitated acids, obtained by partial stepwise oxidation of Aleksinac (Yugoslavia) shale kerogen, were studied by thermal analysis. Significant differences were observed in the weight loss and the shape of TG curves of precipitated acids from various degradation steps, indicating their structural differences and heterogeneity of the kerogen. The thermal curves of precipitated acids were found to consist of two distinct parts. From IR data it was found that the low-temperature part corresponded to thermal changes of aromatic, and the high-temperature part of aliphatic type structures. These results were in good agreement with chemical analysis (elemental analysis, atomic H/C ratio, total acidity) of the same acids.

Many investigators have attempted to establish the chemical nature of kerogen. The main difficulties in such studies result from the macromolecular nature of kerogen and consequently from its insolubility. Therefore, most of the structural studies require a degradation of kerogen into identifiable fragments. Stepwise oxidative degradation of kerogen with alkaline permanganate has often been used in structural studies of kerogens [1-3]. Neutral and basic products (Fig. 1) are generally obtained in very low yields. Ether-soluble acids obtained in higher yields (Fig. 1), were found to be suitable for further GC-MS investigations. Precipitated acids were usually obtained in highest yields. Being still of relatively high molecular weight they have retained much of kerogen structural characteristics. However,

* Paper presented at the World Conference on Thermal Analysis, Madeira (Portugal), 1986.

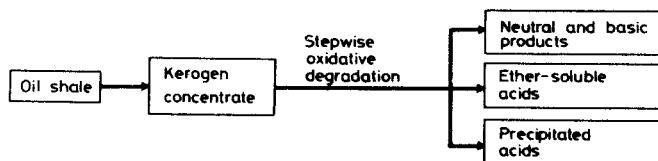


Fig. 1 General experimental scheme

they are not soluble in water and organic solvents which restricts the use of most instrumental analytical methods for their structural investigations.

It was supposed that TG could be useful in characterizing the precipitated acids and consequently for structural characterization of the precursor kerogen itself. Only a few papers have been published on the application of TG and associated techniques to kerogen. One such paper was a review by Durand-Souron [4]. The presence of inorganic materials and the heterogeneity of the kerogen were shown to make the interpretation of the results of TG difficult. By contrast, it seemed to us that it should be useful to apply TG for the study of precipitated acids which are more homogeneous and less complex than their precursor kerogen.

Experimental

Oil shale sample. Preparation of kerogen concentrate

The experiments were carried out with a lacustrine Miocene sediment, oil shale from Aleksinac (Yugoslavia). A kerogen concentrate was prepared from the powdered shale sample (– 100 mesh, Tyler) by successive treatment with benzene (72 hr), hydrochloric acid (1 : 10), benzene (36 hr), potassium hydroxide in methanol (24 hr), a hydrochloric-hydrofluoric acid mixture (1 : 1), distilled water and, finally, a benzene-methanol mixture (1 : 1, 3 × 36 hr). The resulting kerogen concentrate consisted of 72.40% kerogen (by difference), 26.50% pyrite and 1.10% non-pyritic mineral matter. The elemental composition of the organic material is shown in Table 1.

Oxidative degradation. Precipitated acids and methods for their analysis

A stepwise alkaline permanganate degradation method was used in this study. The kerogen concentrate was partially oxidized at 75° in 12 steps with 0.50 g portions of KMnO_4 in alkaline solution, according to a procedure described elsewhere [5, 6]. In the first step 3.3448 g of the kerogen concentrate was dispersed in 100 cm³ 1.6% KOH heated to 75° and the first portion of permanganate was added.

After the reduction of the permanganate, the alkaline solution was separated by centrifugation and the following degradation products were isolated: neutral and basic products, ether-soluble acids and precipitated acids [5]. The solid residue was dispersed again in 100 cm³ 1.6% KOH and a new portion of permanganate was added. The same procedure was repeated until the total of 12 portions of permanganate had been added. Alkaline solutions from some of degradation steps were combined (from steps 2 and 3; 4, 5 and 6; 7, 8 and 9; 10, 11 and 12) and the precipitated acids isolated from them were designated PA-2, PA-3, PA-4 and PA-5, respectively. Precipitated acids from the first degradation step were designated PA-1. The general procedure is shown in Fig. 2.

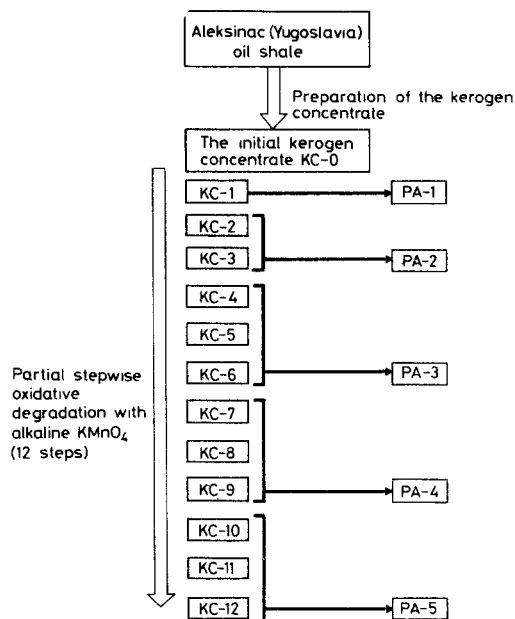


Fig. 2 General degradation scheme: Isolation of precipitated acids (PA) and of partially degraded kerogen concentrates (KC)

The total acidity of the precipitated acids was determined by usual chemical method [7]. The calculated values of acid numbers were shown in Table 1.

Thermogravimetric analyses (20–900°) were carried out with a DuPont 951 thermogravimetric analyser (plug-in module for the DuPont 990 Thermal Analyser). The ambient atmosphere was argon and its flow rate was 15 cm³/min. The size of the sample was about 10 mg and the heating rate was 5 deg/min.

IR spectra were obtained on a Perkin–Elmer 457 spectrometer.

Results and discussion

Chemical analysis

The precipitated acids from various degradation steps differed considerably in elemental composition, atomic H/C ratio and acid number (Table 1).

Table 1 Chemical characteristics of the initial kerogen concentrate (KC—O) and the precipitated acids

Sample	Acid number	Atomic H/C ratio	Elemental analysis				
			% C	% H	% N	% S	% O (by diff.)
KC—O	—	1.19	68.79	6.89	2.46	—	—
PA-1	233.4	0.76	60.46	3.83	2.98	2.64	30.09
PA-2	210.3	1.00	62.25	5.22	3.69	2.54	26.35
PA-3	192.9	1.15	64.96	6.30	4.13	2.57	22.04
PA-4	178.4	1.26	67.17	7.12	3.65	1.88	20.18
PA-5	137.8	1.38	66.48	7.71	3.68	1.82	20.31

A gradual increase in the atomic H/C ratio for the precipitated acids towards the later steps indicated an increase in the share of aliphatic-type material. This corroborated our earlier findings [3, 5] that the Aleksinac (Yugoslavia) shale kerogen was composed of two major types of organic material differing in chemical nature and origin: an aliphatic-type material, more resistant towards alkaline permanganate, and a more susceptible aromatic (coaly)-type material. Moreover, in several degradation studies it was demonstrated that the precipitated acids from the first degradation steps mostly originate from the degradation of aromatic-type material, while those from the later steps stem from aliphatic-type material. IR spectra supported such structural interpretation. Absorption bands of aliphatic groups ($\geq\text{CH}$ 3000–2800; >CH_2 and $-\text{CH}_3$ 1475–1430 cm^{-1}) were more pronounced for PA-5 than for PA-2 (Fig. 3). The ratio of the aromatic (1640 cm^{-1}) and carbonyl (1730 cm^{-1}) peaks was considerably higher for PA-2 than for PA-5.

This clearly indicated that in the later steps progressively larger shares of kerogen aliphatic structures were degraded.

Thermogravimetric analysis of kerogen and precipitated acids

The results of DTG analyses of the initial kerogen concentrate (KC—O) and the precipitated acids are shown in Fig. 4. Considerable differences between the thermal

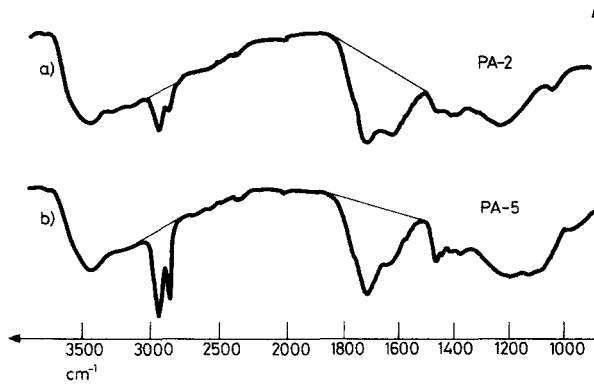


Fig. 3 IR spectra of the precipitated acids: A) PA-2; B) PA-5

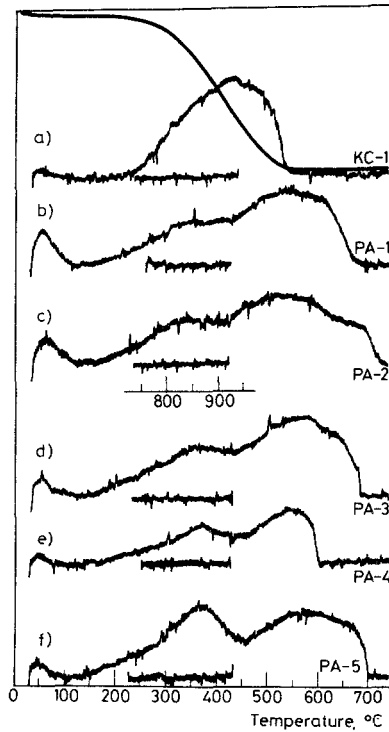


Fig. 4 DTG of the kerogen and corresponding partially oxidized samples. A) Kerogen; B) PA-1; C) PA-2; D) PA-3; E) PA-4; F) PA-5

curves of the kerogen and those of the precipitated acids were observed. They were reflected in the thermal stability and in the shapes of the peaks. The thermal curves of the precipitated acids consisted of clearly-defined low-temperature (250–500°) and high-temperature (450–700°) parts. These two parts could hardly be recognized in the DTG curve of the kerogen. In addition, for the precipitated acids the high-temperature part was shifted towards higher temperatures. Thus, the decomposition of the precipitated acids was finished at 650–700°, while the decomposition of the kerogen ended at only 550°.

The effects of progressive oxidation could be recognized in the curves of the precipitated acids. The intensity of the low-temperature part constantly increased compared with the high-temperature part for the series PA-1 to PA-5. The ratio of the corresponding areas increased from 0.6 (PA-1) to 1.0 (PA-5). Besides these changes, the high-temperature and low-temperature parts were better resolved for PA-4 and PA-5, as a result of complete disappearance of the middle fraction (400–500°) observed earlier in the samples PA-1, PA-2 and PA-3, probably as a result of oxidation of some structural fragments of precipitated acids.

According to the DTG curves obtained, a temperature of 450–460° could be taken as a border line between the low-temperature and high-temperature regions. In order to investigate the structural changes which correspond to the low-temperature peaks, samples of PA-2 and PA-5 were heated in the DuPont 990 Thermal Analyzer from 20 to 460° and kept for one hour at 460°. The IR spectra of the residues obtained are shown in Fig. 5. Only aromatic (1620 cm^{-1}) and carbonyl (1720 cm^{-1}) peaks were observed. These results confirmed that the low-temperature part corresponded to aliphatic, and the high-temperature part to aromatic structures. The results of TG corroborated the inhomogeneity of the kerogen from Aleksinac shale. In spite of the similar general shapes of the peaks in the aromatic part, a pair of completely identical thermal curves could not be found. How much this is a result of real inhomogeneity or of the limited and thus progressive diffusion during oxidation is not clear.

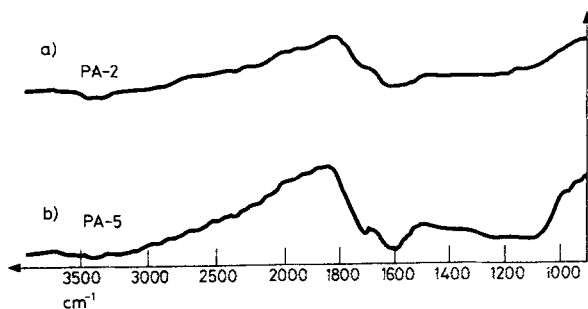


Fig. 5 IR spectra of the samples PA-2 and PA-5 after heating 1 hour at 460°. A) PA-2; B) PA-5

The increased resolution of the peaks of the precipitated acids from the later steps indicated the possible presence of a component (400–500°) readily susceptible to oxidation. This component might have been oxidized first and therefore did not appear in the curve when the sample was completely porous. The absence of this component is apparent in the curve of sample PA-5. Thus, sample PA-4 can be regarded as really porous, and the differences between the thermal curves of PA-4 and PA-5 originated only from the inhomogeneity of the starting kerogen.

Shapes of the thermal curves

The DTG curve of kerogen from Aleksinac shale has a complex structure (Fig. 6) and does not belong to any of the types in the classification of Durand-Souron [4]. Computer analysis of the DTG curve (resolution to Gaussian curves) indicated the presence of at least five groups with different thermal properties (Fig. 6).

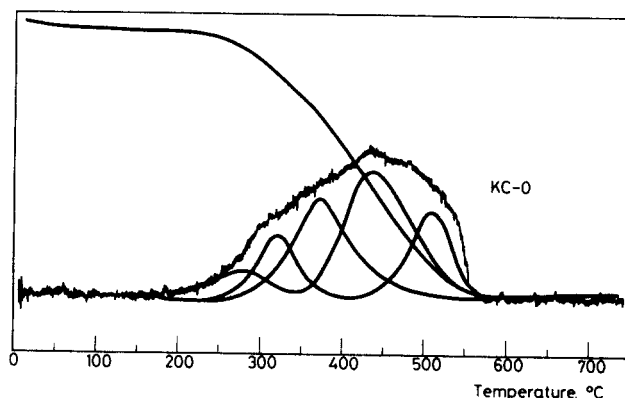


Fig. 6 Computer analysis of a shape of the DTG curve of kerogen sample

Consequently, the Aleksinac shale kerogen analyzed could be a combination of type I and type II (Durgand-Souron classification), or, more probably, is a new type with complex properties.

The thermal curves of the precipitated acids were complex in a similar way (Fig. 7). The aliphatic part was composed of two, and the aromatic part of three components. The same numbers of components present in the initial kerogen and in the precipitated acids indicated their structural relationship. For an analysis of the mathematical shape of the curves, partial thermogravimetric analysis (PDTG) is necessary, while for a study of the chemical nature of the present compounds, some of the combined physical-chemical methods (IR-HPLC) could be used.

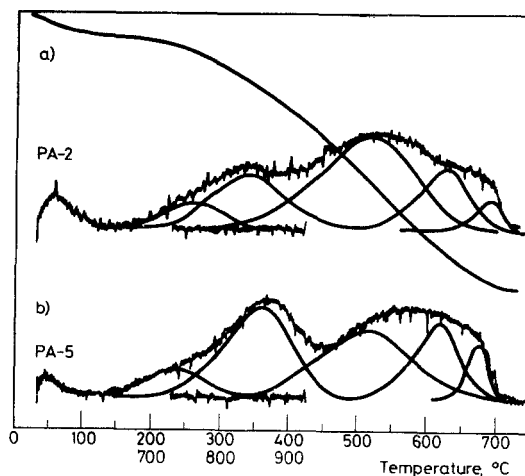


Fig. 7 Computer analysis of a shape of partially oxidized precipitated acids. A) PA-2; B) PA-5

References

- 1 M. V. Djuričić, D. Vitorović, B. D. Andresen, H. S. Hertz, R. C. Murphy, G. Preti and K. Biemann, *Adv. in Org. Geochem.*, 1971 (ed. by H. R. von Gaertner and H. Wehner), Pergamon Press, Oxford, 1972, pp. 305–321.
- 2 D. Vitorović and M. Djordjević, *Bull. T. LXXX de l'Académie Serbe des Sciences et des Arts, Sciences Naturelles No. 22* (1982) 15.
- 3 D. Vitorović, M. V. Djuričić and B. Ilić, *Adv. in Org. Geochem. 1973* (ed. by B. Tissot and F. Bierner) Edition Technip, Paris, 1974, pp. 179–189.
- 4 C. Durand-Souron, in: *Kerogen-Insoluble Organic Matter from Sedimentary Rock* (ed. by B. Durand), Editions Technip, Paris, 1980, pp. 143–161.
- 5 V. D. Krsmanović, M. Ercegovac and D. Vitorović, *Org. Geochem.*, 1 (1978) 85.
- 6 D. Vitorović, V. D. Krsmanović and P. Pfendt, *Adv. in Org. Geochem. 1979* (ed. by A. G. Douglas and J. R. Maxwell) Pergamon Press, Oxford, 1980, pp. 585–589.
- 7 V. D. Krsmanović and D. Vitorović, 3rd Yugoslav Symposium on Organic Chemistry, Ljubljana, 1984; Abstract of papers, pp. 152–153.

Zusammenfassung — Durch partielle schrittweise Oxydierung von Schieferkerogen (Aleksinac, Jugoslavien) erhaltene präzipitierte Säuren werden thermoanalytisch untersucht. Signifikante Unterschiede wurden im Gewichtsverlust und der TG-Kurvengestalt von nach den einzelnen Abbauschritten erhaltenen präzipitierten Säuren beobachtet, was auf deren strukturelle Verschiedenheit und auf die Heterogenität des Kerogens hinweist. Die thermische Kurven der präzipitierten Säuren weisen zwei sich unterscheidende Abschnitte auf. Aus IR-Daten ergab sich, daß im Tieftemperaturabschnitt thermische Veränderungen von aromatischen, im Hochtemperaturabschnitt dagegen von aliphatischen Strukturen verlaufen. Diese Ergebnisse stimmen mit chemischen Analysendaten (Elementaranalyse, H/C-Atomverhältnis, Gesamtsäure) gut überein.

Резюме — С помощью термического анализа изучены осажденные кислоты, полученные путем частичного ступенчатого окисления сланцевого керогена месторождения Алексинац (Югославия). Значительные различия, наблюдаемые в потере веса и форме кривых ТГ осажденных кислот, полученных на различных стадиях разложения керогена, свидетельствуют о его гетерогенности и структурном различии. Наблюдали, что термические кривые осажденных кислот состоят из двух различных частей. На основе ИК спектров установлено, что низкотемпературная часть соответствует термическим изменениям ароматических компонент, тогда как высокотемпературная часть — алифатических компонент. Полученные результаты хорошо согласуются с данными химического анализа (элементный анализ, атомное соотношение водород-углерод, общая кислотность) тех же самых кислот.