

Kerogenization of Asphaltenes by Air Oxygen: The Heimar (bold Petroleum Seepage) Sandstone from the Dead Sea Basin (Israel)

Pavle I Premović, Jorgovanka R Bojić and Ivana R Tonsa

Laboratory for Geochemistry and Cosmochemistry, Faculty of Science
University of Niš, PO Box 91, 18000 Niš, FR Yugoslavia

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Kerogen-like material was generated during a laboratory heating experiment with asphaltenes in the presence of air oxygen. Asphaltenes were extracted from a Heimar (A recent seep) and IPRG sandstones (Dead Sea Basin, Israel) impregnated by heavy/asphaltic crudes and heated at 100-200 °C for 1-12 d. The (pseudo*)-activation energy (E_a) is calculated to be ca. 10 kcal mol⁻¹ K⁻¹. Therefore, half-life $t_{1/2}$ (i.e.) the time of conversion of 50 per cent of Heimar A asphaltene into artificial kerogen is estimated to be ca. 2000 d (0 °C); 700 d (15 °C); 400 d (25 °C); 150 d (35 °C); and, 100 d (50 °C). These results suggest the possible occurrence of low temperature (≤ 100 °C) kerogenization by air oxygen of the Dead Sea asphaltenes as one of the formation pathways of kerogen-like material associated with the Heimar sandstone (Bold petroleum seepage location) impregnated with a heavy crude.

Introduction

It is generally concluded that kerogen and associated asphaltenes originate from the same precursor(s). Asphaltenes are smaller molecules containing fewer crosslinkages than kerogen. Hence, kerogen is always solid and insoluble in organic solvents but asphaltenes can be brought into (colloidal) solution. Structurally, asphaltenes are similar to kerogen.¹⁻⁵

Crude oil generation from a source rock is probably a two-step process. Kerogen in a source rock can be thought of as several asphaltene molecules held together by weak bonds. At low temperatures these bonds in kerogen are ruptured, producing asphaltenes. With increasing temperatures, these disintegrate further to produce petroleum. In addition, asphaltenes may arise as a result of alteration of petroleum caused by water-washing, incipient biodegradation or physical loss of volatile components (devolatilization).⁶

Surprisingly, hardly any consideration has been given to asphaltenes as a potential source of coexisting amorphous kerogen. Recent work by Premović *et al.*⁷ on thermal stability of vanadyl (VO²⁺) porphyrins (P) in the asphaltene fraction extracted from Dead Sea (DS) floating asphalt has indicated that amorphous kerogen-like

material can be isolated from this asphaltene material when heated at 100-200 °C in air. For this reason, asphaltenes were extracted from the Heimar (A recent seep) and IPRG sandstones and heated up to 200 °C in air.

The present work aims at carrying out the oxygenic kerogenization of the Heimar A and IPRG asphaltic crudes and to evaluate the probability that kerogen within the Heimar B (old seep) is derived for surficial heating of the asphalt in air atmosphere.

Experimental

Samples

Petroleum of various forms have been found in a small area around the DS. Extra-heavy crudes (asphalts) occur in the DS area on the surface as well as in depth (up to 3600 m).⁸ A detailed description of the samples and their locations are given elsewhere.⁹⁻¹³ Geological map (the various samples considered are marked) is presented in Figure 1.

Extraction and Separation

Powdered (to pass 100 mesh) bituminous sandstones were treated with boiling HCl (6M) to remove most of the carbonates. The insoluble residue was demineralized further by a repeated treatment with an HF/HCl mixture

*i.e. the energy of the overall reaction pertaining to the intense generation of artificial kerogen

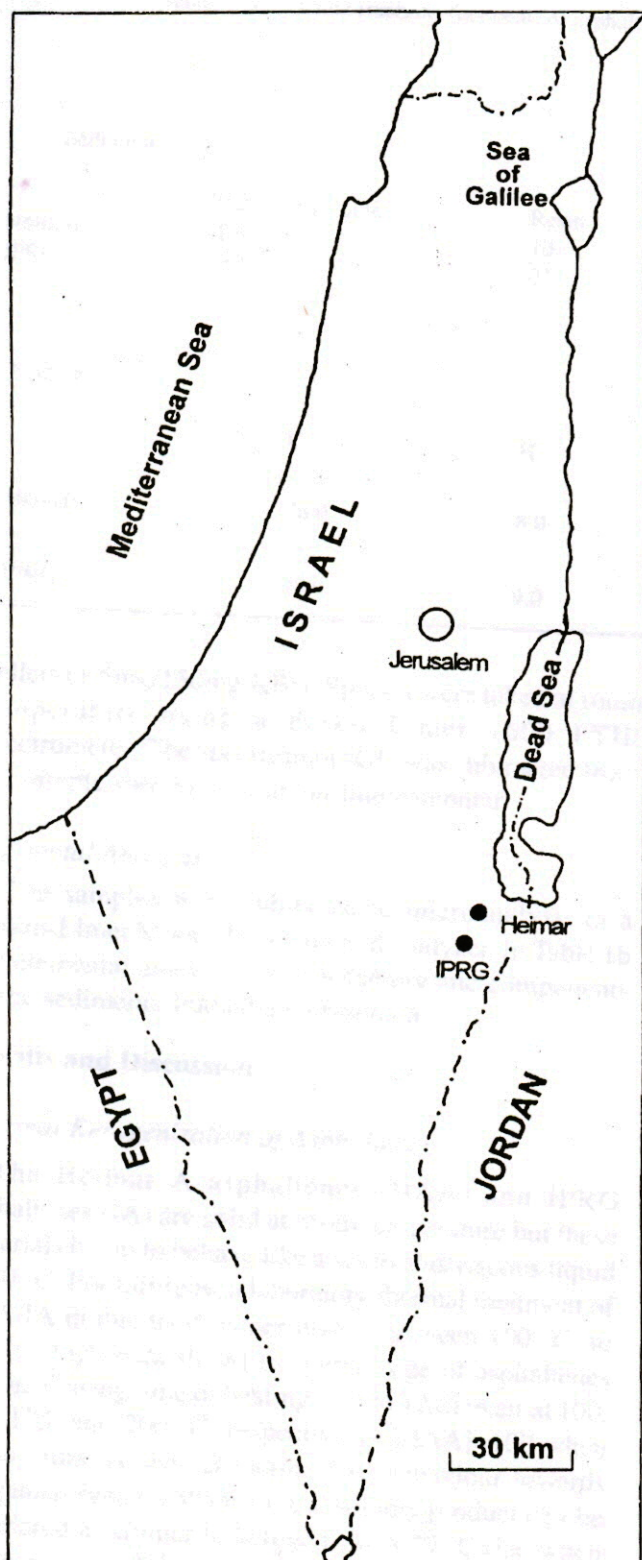


Figure 1 — Geological map indicating sample locations (after Bentor et al.²⁸)

(22M and 0.25M, respectively). This acid mixture removes silica. The insoluble residue (organic fraction + insoluble inorganic minerals) was treated with benzene (Soxlet) for 48h. The soluble fraction was centrifuged for 2h and the supernate was filtered. After removal of benzene by vacuum evaporation, the residue was weighed in a 150ml polyethylene bottle. 100ml *n*-hexane was then added and the bottle shaken for 4h at room temperature to precipitate the asphaltene fraction. The solution was centrifuged and asphaltenes were washed several times with *n*-hexane until the wash solution was clear. Asphaltenes were then dried under nitrogen at 45 °C to remove the solvent and the precipitation with *n*-hexane was repeated. The small amount of asphaltenes precipitated was combined with the bulk of asphaltenes. The maltene fraction was recovered by evaporation of *n*-hexane and was then extracted with 35ml of anhydrous methanol for 8h. The solution was centrifuged and the precipitated resins extracted twice with methanol. The methanol was evaporated to obtain the methanol (soluble) fraction. Kerogen like material was separated from acid-resistant mineral grains in the residue by the chloroform sink-float technique.¹⁴ The kerogen, asphaltene, resin and methanol fractions were weighed and the proportions of the three fractions were determined, Table 1a.

Heating Experiments

Heating experiments of extracted asphaltenes were conducted as follows: Sets of 50-100 mg of asphaltenes were put into glass tubes (4 mm i.d., 15 cm long) at room temperature. Each tube was heated in an electric furnace at temperatures ranging from 50 to 200 °C, for 1 to 30 d. For the experiments in the absence of air the glass tubes were evacuated (ca 10 mm Hg) and then flushed with N₂ and sealed. It is important to emphasize that the trace (about 10 ppm) of O₂ left in the sealed sample tubes after their evacuation was quickly and thoroughly exhausted by oxidation of carbonaceous material during laboratory heating. After heating, the reaction products were separated into a fraction soluble in a benzene:methanol (3:1 v/v) mixture (asphaltenes) and insoluble part (kerogen). The amount of soluble material was determined by the weight difference by solvent extraction, and the amount of kerogen was determined by weighing the residue obtained after solvent extraction.

Fourier Transform (FT) Infrared (IR) Spectrometry

Carbonaceous samples were powdered finely and dispersed evenly in anhydrous potassium bromide (KBr)

Table 1—(a) Organic fractions (per cent) of asphaltic crudes and (b) elemental analysis (wt per cent) of asphaltic crudes

Sediment	(a)		
	Methanol-soluble	Resin	Asphaltene
Heimar	64	13	22
IPRG	10	25	65

Sample	(b)				
	C	H	N	S	O
Heimar	76.0	8.0	2.0	9.0	5.0
IPRG	78.0	9.0	1.0	8.0	4.0

pellets (1.5mg/150mg KBr). Spectra were taken at room temperature using a Perkin-Elmer 1600 FTIR spectrometer. The spectrum of KBr was subtracted from the sample spectrum by an on-line computer.

Elemental Analysis

The samples were subjected to microanalysis in a Perkin-Elmer Model 240 elemental analyzer. In Table 1b the elemental analysis data for the organic components of the sediments studied are presented.

Results and Discussion

Thermal Kerogenization of Asphaltenes

The Heimar A asphaltenes (HAA) and IPRG asphaltenes (IA) are solid at room temperature but these materials begin to behave like a semisolid/viscous liquid at 70 °C. For this reason laboratory thermal treatment of HAA/IA in this work is performed between 100 °C to 200 °C. Figure 2a shows the percentage of asphaltenes with increasing time of heating (t=1 to 12 d) in air at 100, 150, 175, and 200 °C, respectively ([HAA]=100 when heating time is t=0). Because of its behaviour towards inorganic/organic solvents the insoluble product can be considered as similar to kerogen. At <70 °C (i.e. when asphaltenes is solid) and in the accessible period of time, generation of kerogen-like product did not occur to any measurable extent. It can be seen from Figure 2a that these ratios remain constant (within experimental error)

and close to those of the parent asphaltenes. In fact, H/C and O/C values (Figure 3a and b, respectively) of the material in question are typical for kerogen as defined.¹⁵ Similar results were obtained for IA. Hereafter, kerogen produced from heat-treated asphaltenes (up to 200 °C) in the presence of air will be referred to as "asphaltene-derived kerogen" (AK). We shall use throughout this paper the term "kerogenization" for thermal conversion of HAA/IA (or similar asphaltenes) into kerogen-like material.

Role of O₂ in Kerogenization of HAA/IA

Having no internal physical structure, it is reasonable to assume that (amorphous) AK is derived through oxidative polycondensation/polymerization processes of a random nature. On the other hand, kinetic results suggest that air may play an important role in laboratory thermal conversion of asphaltenes into AK. In separate experiments, it was also demonstrated that the active component of air is O₂, since pure O₂ at a pressure corresponding to the partial pressure in air was equally effective.

Bulky asphaltenes are immobile from room temperature to 200 °C (ref. 16). Consequently, the physical state of asphaltenes within this temperature range has no/little effect on the kinetic parameters of the asphaltenes kerogenization which depend on molecular motion, but it does affect the diffusion of atmospheric O₂ through the asphaltenes matrix. However, the diffusion rate of O₂ into

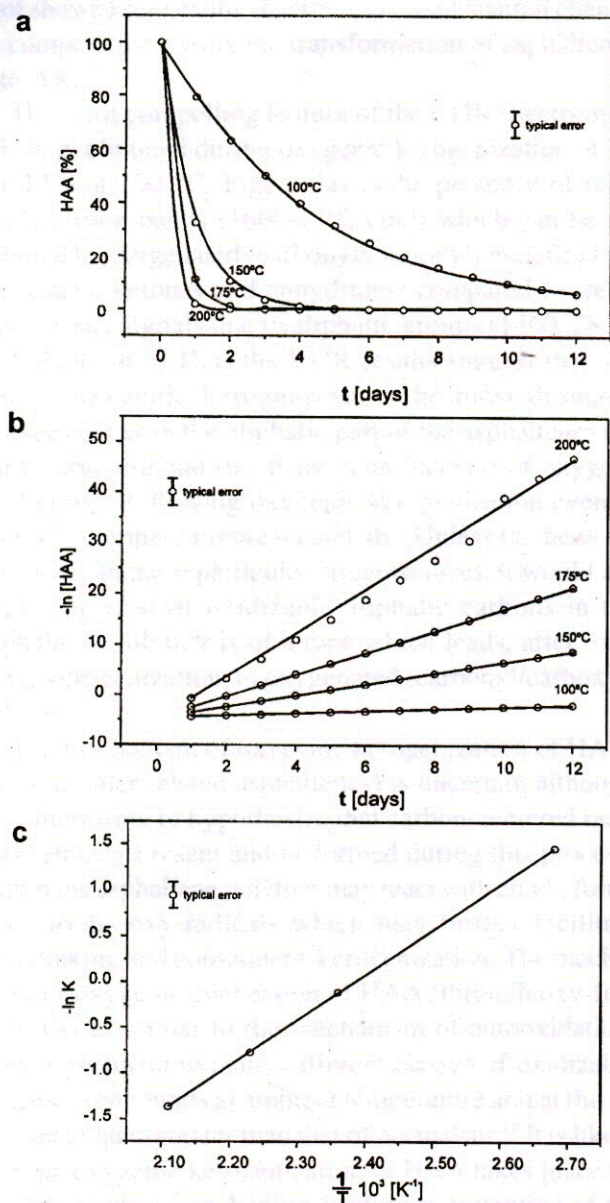


Figure 2 — The amount of HAA ([HAA]) on heating at 100, 150, 175 and 200 °C for 1 to 12 d: (a) in the presence of the air atmosphere; (b) plots of decreasing rates of HAA according to first-order reaction; (c) The Arrhenius plot of decreasing rates of HAA.

the interior of liquid asphaltene is relatively high ($t_{1/2} < 100\text{ms}$)¹⁷, thus we may safely postulate that this process is not a rate-determining step in the oxygenic kerogenization of asphaltenes.

The FTIR spectrum of AK obtained through heating in the presence of O_2 of HAA/IA either at 100 °C (Figure 4a) or at higher temperatures shows principal bands at 750 to 850 cm^{-1} (a succession of weak bands related to various aromatic CH); 1380 cm^{-1} (a moderate band ascribed to CH_3); 1460 cm^{-1} (a strong band related to linear/

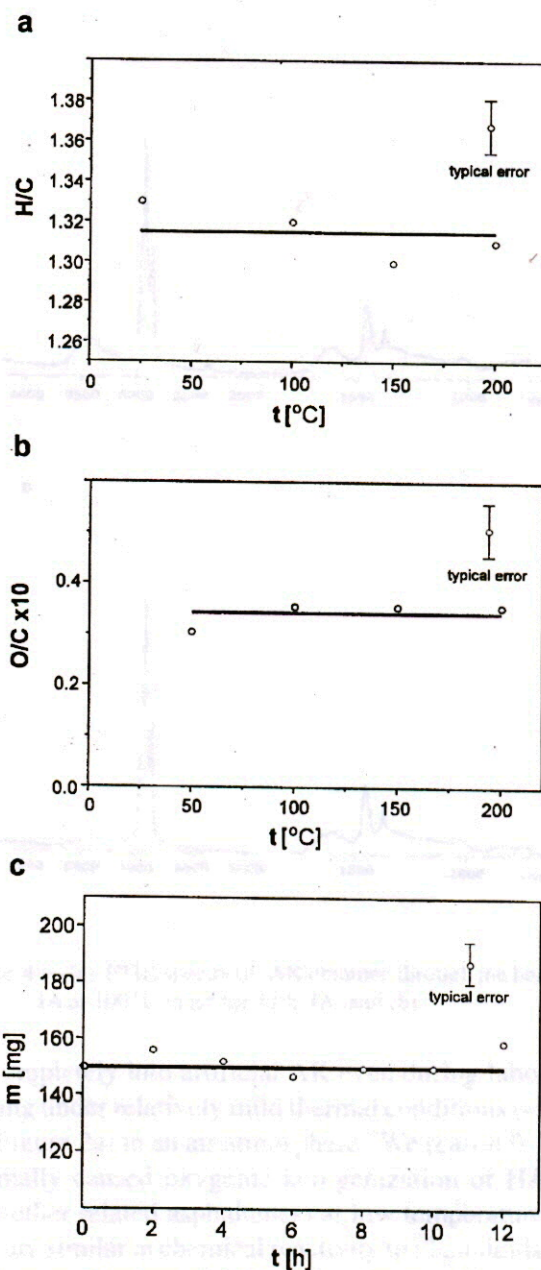


Figure 3 — (a) The atomic H/C and (b) O/C ratios of HAA/AK obtained on heating at various temperature for 1 to 12 d in the presence of air O_2 ; (c) mass variation of the HAA sample vs. heating time on 100 °C

cyclic CH_2 groups); moderate bands (1600 to 1200 cm^{-1}); associated with oxygenated groups; 2850 cm^{-1} and 2920 cm^{-1} (two strong bands attributed to aliphatic CH_2/CH_3 functions) with a shoulder near 2960 cm^{-1} characteristic of ample chain branching. Assignments for FTIR bands are based on the work of Rouxhet and Robin¹⁸ on kerogen. Qualitatively, this spectrum (Figure 4a) is similar to the spectrum of IA (i.e. HAA) (Figure 4b) or HAA

(not shown) suggesting that there is no substantial change in composition during the transformation of asphaltenes into AK.

The most compelling feature of the FTIR spectrum of AK (e.g. obtained during oxygenic kerogenization of IA for 12 h at 100 °C, Figure 4a) is the presence of relatively strong bands (1600-1700 cm^{-1}) which can be attributed to oxygenated (carbonyl/carboxyl) moieties (acids, esters, ketones and anhydrides) compared to relatively weak signals due to aliphatic groups (1460, 2850, and 2929 cm^{-1}). Thus the FTIR results suggest that: (a) during oxygenic kerogenization the most dramatic changes occur in the aliphatic part of the asphaltenes organic structure and (b) there is an increase of oxygenated groups following oxygenic kerogenization even at 100 °C (compare Figure 4a and 4b). Unless O_2 behaves unusually in these particular circumstances, it would appear that most of oxidizable aliphatic carbons in the asphaltene polymer is of a type which leads, after oxygenic kerogenization, to oxygenated (carbonyl/carboxyl) structures.

The mechanism of oxygenic kerogenization of HAA/IA (and other related asphaltenes) is uncertain although it is interesting to hypothesize that carbon-centered radicals (already present and/or formed during this process) within the asphaltene polymer may react with air O_2 , forming various oxy-radicals which may further facilitate crosslinking and consequent kerogenization. The mechanism of oxygenic conversion of HAA (through oxy-free radicals) is similar to the mechanism of autooxidation. This is pertinent to many different classes of oxidizable organic compounds at ambient temperature and at the O_2 pressure equal/greater than that of normal air.¹⁹ It is likely that the oxygenic kerogenization of HAA takes place by an initial radical mechanism leading to formation of organic (hydro)peroxides and changes occurring during this process may be interpreted in terms of autooxidation reactions with subsequent formation of AK as a final product. It may, however, be noted that the rate of oxygenic kerogenization of asphaltenes depends on the oxygen pressure. In principal, this could be due to the initiation of kerogenization chains by air O_2 , but this source of initiation is generally insignificant. On the other hand, it is likely that oxygen atoms are the main crosslinking factor between the asphaltene molecules in the oxygenic kerogenization.

The most intriguing result of this study is that almost the entire HAA/IA is kerogenizable under suitable physicochemical conditions, i.e., it is possible to convert HAA/

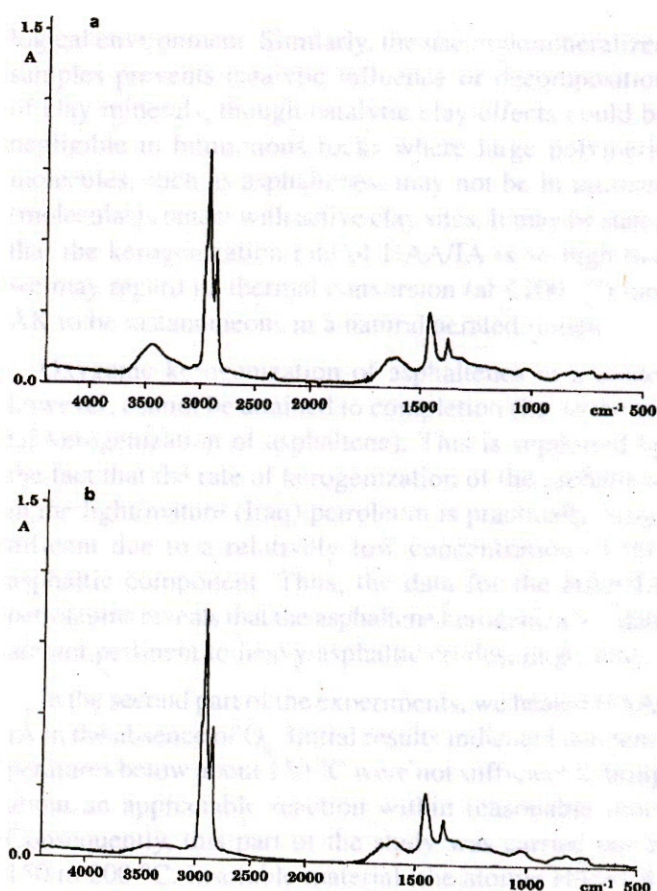


Figure 4 — (a) FTIR spectra of: AK obtained through the heating of IA at 100 °C in air for 12 h IA and (b)

IA completely into artificial AK even during laboratory heating under relatively mild thermal conditions (e.g. 100 °C, Figure 2a) in an air atmosphere. We reason from the thermally caused oxygenic kerogenization of HAA/IA (and other related asphaltenes) at low temperatures that they are similar in chemical reactivity to plant lipids (generally polyunsaturated fatty acid moieties). Many chemical studies indicate that these compounds have the capability to polymerize into kerogen-like matter under mild thermal conditions in either absence²⁰ or the presence²¹ of atmospheric oxygen.

In general, petroleum asphaltenes are thought to be heterogeneous polymeric material containing varying proportions of the saturate/unsaturate moieties, with average molecular weight of up to several thousands^{22,23} (and references cited therein).²⁴ It may be tentatively suggested that the unsaturated structures play an essential role in oxygenic kerogenization of asphaltenes. Evidently, the number of these structures of HAA/IA is too low to

be detected by FTIR approach. Strausz *et al.*²⁵ have suggested (from the available data reported to date) that a very substantial proportion of the mass of the petroleum asphaltenes, in general, originated from *n*-alcanoic (probably fatty acids) precursors by thermocatalytic cyclization/aromatization.

The Kerogenization Kinetics of HAA

Figure 3c shows that the weight of the HAA sample is constant (within experimental error) during laboratory oxygenic kerogenization at 100°C for 12 d. It is argued that: (a) reaction pathways leading to evolution of CO, CO₂ and water are not important during oxygenic kerogenization at ≤100 °C and (b) oxygenic kerogenization at ≤100 °C is, chemically speaking, rather a mild chemical process.

To estimate the rate of kerogenization of HAA, we model this process by a first order reaction and obtain Eq. (1).

$$-\ln [\text{HAA}] = kt - \ln 100, \quad \dots(1)$$

where *k* is a rate constant. Therefore, the plot of the logarithmic amount of HAA (ln [HAA]) against *t* gives a straight line. Figure 2b shows the experimental results. Although experimental values are delimited, a straight line can be approximated at different temperatures from 100 to 200 °C. The rate constants (calculated from the slope of the lines in Figure 2b) are plotted vs temperature (1/T[10³ K⁻¹]) as shown in Figure 2c. The points approximately conform to Eq. (2).

$$-\ln k = 0,5 E_a / T - 12,2, \quad \dots(2)$$

where *k* is a rate constant (d⁻¹). The (pseudo-)activation energy (*E_a*) is calculated to be ca. 10 k cal mol⁻¹ K⁻¹. Therefore, half-life *t*_{1/2} (i.e. the time of conversion of 50 per cent of HAA into AK) is estimated to be ca. 2000 d (0°C); 700 d (15 °C); 400 d (25 °C); 150 d (35 °C); and, 100 d (50 °C).

It may, however, be emphasized that all kinetic data presented here are approximate estimates and cannot be directly applied to geological situation because *in vitro* kerogenization of asphaltenes could be into different from that in the natural DS environment. We should, however, evaluate the roles of heating rate, water and other (than asphaltenes) geoorganic materials on the kerogenization of asphaltenes in order to approach the conclusion of the timing of the asphaltenes conversion into AK in a geo-

logical environment. Similarly, the use of demineralized samples prevents catalytic influence or decomposition of clay minerals, though catalytic clay effects could be negligible in bituminous rocks where large polymeric molecules, such as asphaltenes, may not be in intimate (molecular) contact with active clay sites. It may be stated that the kerogenization rate of HAA/IA is so high that we may regard its thermal conversion (at ≤100 °C) into AK to be instantaneous in a natural aerated milieu.

Oxygenic kerogenization of asphaltenes in a crude, however, cannot be attained to completion (i.e. to the total kerogenization of asphaltene). This is supported by the fact that the rate of kerogenization of the asphaltene in the light/mature (Iraq) petroleum is practically insignificant due to a relatively low concentration of this asphaltic component. Thus, the data for the HAA/IA petroleums reveals that the asphaltene kerogenization data are not pertinent to heavy/asphaltic crudes, in general.

In the second part of the experiments, we heated HAA/IA in the absence of O₂. Initial results indicated that temperatures below about 150 °C were not sufficient to bring about an appreciable reaction within reasonable time. Consequently, this part of the study was carried out at 150 to 200 °C. Insoluble material (the atomic H/C=1:4) generated at ≤ 200 °C indicates that it may also be characterized AK. Kinetic data show that the amount of AK produced during heating in air (Figure 2a) is significantly higher than that generated in the absence of air for temperature ranges administered.

The kerogenization rate of HAA/IA in the absence of O₂ is much slower than in the presence of O₂. Unfortunately, the difference in rates of anaerobic kerogenization at 150°C to 200 °C was not much, making the determination of *k* practically impossible. Our kinetic considerations indicate that the anaerobic AK generation reaction has complex high-order reaction kinetics, i.e., the major extent of the reaction occurs initially (< 10 d). Depending on experiment no/barely discernible reaction extent occurs much longer duration (> 15 d), even for reaction times of month(s). If this reaction is first-order then even at very slow reaction rates, given geologic time, it can proceed to high degree of completion.

Geochemical Implications

Origin of the DS Kerogen in the Heimar B Location

Our kinetic data infer that for a sufficiently long time aerobic kerogenization of asphaltenes in a heavy/asphaltic

crude could be effectively fast especially at/near the surface if it was subjected to common surficial temperatures (≤ 60 °C)¹¹. This is evident from the high kerogen content (19 per cent) of organic fraction of the surficial Triassic sandstone (impregnated mostly by heavy crude) at the Heimar B (old seep location) in spite of (geologically speaking) short duration (less than thousand years and possibly only several hundreds of years) spent at the surface.²⁶ By contrast, organic material (mostly asphaltic crude which is also incorporated into the sandstone structures) of the Heimar A (recent seep location) contains less than 1 per cent of kerogen.²⁶ Most plausible explanation is that the aerobic kerogenization of HAA at the Heimar A site has advanced very little as this material has been exposed to the air at/near the surface for short duration (i.e less than ten years). According to Nissenbaum and Goldberg²⁷, both these materials did migrate from a deep bitumen-bearing zone to the surface.

Conclusions

It is evident from the above results that asphaltenes extracted from the Heimar (A recent seep)/IPRG sandstones generated an insoluble product on laboratory heating in the presence of air O₂ in, geological terms, short duration. This material resembles kerogen isolated from the Heimar B sandstone rocks and it is termed "asphaltene-derived kerogen".

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References

- 1 Tissot B P, *Petroleum Geology in China*, edited by J F Mason (Penwell Books) 1981,71.
- 2 Tissot B P, *Am Assoc Pet Geol Bull*, **68**(1984)545.
- 3 Bandurski E, *Ener Sources*, **6**(1984),47.
- 4 Pelet R, Behar F & Monin I C, *Org Geochem*, **10**(1986),481.
- 5 Solli H & Leplat P, *Org Geochem*, **10**(1986)313.
- 6 Connan I, in *Advances in Petroleum Geochemistry*, edited by J Brooks and D Welte (Academic Press, New York) Part1,1984,299.
- 7 Premovic P I, Zlatkovic S B, Premovic M P & Tonsa I R, *J Pet Geol*, **21** (1998) 289.
- 8 Nissenbaum A, *Am Assoc Pet Geol Bull*, **62**(1978) 837.
- 9 Tannenbaum E, Starinsky A & Aizenshtat Z, *Am Assoc Pet Geol Stud Geol*, **25**(1987)221.
- 10 Rullkötter I, Spiro B & Nissenbaum A, *Geochim Cosmochim Acta*, **49**(1985)1357.
- 11 Tannenbaum E & Aizenshtat Z, *Org Geochem*, **6**(1984)503.
- 12 Tannenbaum E & Aizenshtat Z, *AAPG Research Conference on Exploration for Heavy Crude Oil and Bitumen*, Preprint, Santa Maria, 1984.
- 13 Tannenbaum E & Aizenshtat Z, *Org Geochem*, **8**(1985) 181.
- 14 Mckirdy D M & Powel T G, *Geology*, **2**(1974)591.
- 15 Tissot B P, Durand B, Espitalie I & Combaz A, *Am Assoc Pet Geol Bull*, **58**(1974)449.
- 16 Kivelson D & Lee S K, *J Chem Phys*, **41**(1964)1896.
- 17 Niizuma S, Steele C T, Gunning H E & Strausz O P, *Fuel*, **56**(1977)249.
- 18 Rouxhet P G & Robin P L, *Fuel*, **57**(1978)533.
- 19 Mead J F, *Free Radicals in Biology*, edited by W A Pryor (Academic Press, New York) **1**(1976)68.
- 20 Shioya M & Ishiwatari R, *Org Geochem*, **5**(1983)7.
- 21 Martin J, Quirke E, Shaw G J, Soper P D & Maxwell J R, *Tetrahedron*, **36**(1980)3261.
- 22 Yen T F, *Ener Sourc*, **1**(1975)447.
- 23 Yen T F, Wen C S, Kwan J T & Show E, *Am Chem Soc, Div Fuel Chem Preprint*, **22**(1977)118.
- 24 Mckay J F, Amend P J, Cogswell T E, Harnsberger P M, Erickson R B & Latham D R, *Am Chem Soc, Div Fuel Chem Preprint*, **21**(1977)708.
- 25 Strausz O P, Mojelsky T W & Lown E M, *Fuel*, **71**(1992)1355.
- 26 Spiro B, *Geochemistry and Mineralogy of Bituminous rocks in Israel* Ph D Dissertation, Hebrew University, 1980.
- 27 Nissenbaum A & Goldberg M, *Org Geochem*, **2**(1980)167.
- 28 Bentor Y K, Vroman A & Zak I, *The Geological Map of Israel*, Geological Survey of Israel, Jerusalem, 1970.