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Thermal stability of the asphaltene/kerogen vanadyl porphyrins

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Abstract—Thermal stability of vanadyl porphyrins incorporated into the asphaltene/kerogen structures of the Dead Sea asphalt "float", the La Luna Mara limestone and the Serpiano marl was studied by electron spin resonance (ESR). Comparative studies were also made on alkyl vanadyl porphyrins such as deoxophylloerythroetioporphyrins and (extracted and commercial) etioporphyrins and tetraphenylporphyrin. According to these studies, alkyl vanadyl porphyrins predominate in the asphaltene/kerogen framework. These porphyrins are stable up to 400°C during laboratory heating, but at and above this temperature their content sharply decreases. At 500°C and 600°C, the asphaltene/kerogen vanadyl porphyrins content follows a similar pattern to that at 400°C, except that at 600°C it was reduced to traces in less than 12 h. In addition, it is implied that a high proportion of the asphaltene/kerogen vanadyl porphyrins (< 50% of total amount) are incorporated into the asphaltene/kerogen matrix with relatively higher activation energies.

The asphaltene/kerogen vanadyl porphyrins kinetics during laboratory thermolysis are characterized by a step-wise pattern. This is attributed to thermolytic decomposition/demetallation of the asphaltene/kerogen alkyl vanadyl porphyrins with various energy barriers mediated by free radical intermediates.

A rough extrapolation of pyrolytic data to longer times, based on both the Arrhenius equation and the often-quoted assumptions for the reaction rate decrease, infer that static laboratory pyrolysis of kerogen is irrelevant to natural geological processes characteristic of petroleum genesis. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The discovery of vanadylporphyrins (VO^{2+}-P) in petroleums, shales, coals and bitumens by Treibs (1934) is marked as the beginning of modern organic geochemistry. Treibs (1936) showed that major components were the alkylporphyrins (P), vanadyl-deoxophylloerythroetioporphyrins (VO^{2+}-DPEP) and vanadyletioporphyrins (VO^{2+}-ETIO) as shown in Fig. 1a,b, respectively. With the advent of modern analytical techniques, researchers showed that besides these two major pseudo-homologous series there is also a third minor type: RHODO porphyrins (RHODO) (Yen *et al.*, 1969). These compounds are mainly derived from chlorophylls and bacteriochlorophylls (Baker and Louda, 1986). The VO^{2+}-P in ancient shales can be arbitrarily divided according to their physicochemical properties into the following two groups: extractable alkyl VO^{2+}-P with (a) relatively low molecular weight and (b) relatively high molecular weight (Baker and Louda, 1986). Premović *et al.* (1986) determined the distribution of vanadium (V) and VO^{2+}-P in various fractions of extracts of the La Luna Mara (LLM) and Serpano (Se) rocks by employing a variety of geochemical and spectroscopic techniques: the existence of VO^{2+}-P in kerogen fractions was shown using ESR spec-

trometry. It has been suggested that they are incorporated into the kerogen structures through aliphatic bonds (Mackenzie *et al.*, 1980). Bitumen fractions of these rocks are also characterized by a high concentration of VO^{2+}-P (mostly the DPEP type; Premović *et al.*, 1986).

The asphalts in the Dead Sea (DS) Basin occur in different forms often as huge floating blocks. Aizenshtat *et al.* (1979) analyzed their metallo- and free base porphyrins (1000–1500 ppm) by ultraviolet (UV)-visible (VIS) spectrophotometry and mass spectrometry. According to these authors the major metal porphyrins (≥ 95%) are VO^{2+}-P, mostly of the DPEP type.

According to Aizenshtat *et al.* (1979) the DS floating asphalt contains carboxylated porphyrins. The presence of these pigments in sedimentary rocks has a bearing on the geothermal history of a given sediment. As early as 1934 it was recognized by Treibs (1934) that preservation of carboxylated porphyrins is also dependent on observations that free porphyrins are decarboxylated at temperatures in the range 300°C to 350°C. The reaction occurs at even ≤ 150°C over extended periods (Yen, 1975). Thus, the presence of carboxylated porphyrins in the DS asphalt is evidence that this bitumen has not been subjected to temperatures > 150°C.

Hodgson and Baker (1957), in a study of the thermal removal of porphyrins and V in crude oil, deduced that the first-order rate for the degradation of porphyrins at 358 C was 0.020 h^{-1}, considerably greater than that for the removal of V, 0.013 h^{-1}. The activation energy was 52.5 kcal mol^{-1} (for porphyrin degradation) and 58.6 kcal mol^{-1} (for V removal). The authors concluded that the rate difference between the porphyrin decomposition and V removal would increase at lower temperatures.

Simulated geothermal maturation experiments with the bitumen fraction of the LLM rock (Didyk *et al.*, 1975) showed that VO^{2+}-DPEP to ETIO conversion is approximately half completed in 166 h, at 210 C.

Advances in probe mass spectrometry and high performance liquid chromatography (HPLC) led to the use of VO^{2+}-P in estimating the maturity of source rocks and crudes. The ratio of two types of VO^{2+}-P, i.e. DPEP and ETIO, have been used by many as maturity indicators. To quantify these results, Sundararaman *et al.* (1988) introduced the Porphyrin Maturity Parameter (PMP) = C$_{28}$E/(C$_{28}$E + C$_{32}$D), where C$_{28}$E and C$_{32}$D represent the relative concentrations of a C$_{28}$VO^{2+}-ETIO and C$_{32}$VO^{2+}-DPEP. Recent work suggests that kerogen/asphaltenes contain predominantly VO^{2+}-ETIO, and these are released during (laboratory/natural) thermal cracking of kerogen/asphaltenes (Barwise, 1987; Sundararaman *et al.*, 1988, 1993). These authors claim that the reason for the change in the DPEP/ETIO ratio, or PMP, with maturation, is due to the dilution of pre-existing VO^{2+}-DPEP by its ETIO analog released from kerogen.

According to Sundararaman *et al.* (1988) during the pyrolysis of the Woodford and New Albany (bituminous) shale kerogens, very little change occurred in PMP at temperatures < 300 C but large changes occurred above 400 C. These authors also found that during the pyrolysis of kerogens of the Williston and Joaquin bituminous rocks, little change in PMP occurred below 435 C above which there was a rather marked shift in PMP.

Van Berkel *et al.* 1989a, b) compared the VO^{2+}-P distribution in the bitumen of New Albany shale (U.S.A.) with that isolated from a shale kerogen by sequential pyrolysis (110–450 C). According to these authors, the DPEP/ETIO ratio of VO^{2+}-P is essentially constant between 110 C and 400 C and then decreases to zero at 450 C. At this temperature, decomposition of the VO^{2+}-DPEP and dealkylation of the VO^{2+}-ETIO occur. Results of isothermal pyrolysis experiments at 296 C by Sundararaman (1993) show that the concentration of extractable VO^{2+}-P increases initially and reaches a maximum value at 168 h beyond which it gradually decreases with time. The sample of rock used in this study was from the Monterey Formation (Santa Maria Basin, California, U.S.A.).

Serebrennikova and Mozzhelina (1994) analyzed VO^{2+}-P isolated from Yakutiya petroliferous shale (Russia) bitumen and also from kerogen and bitumen pyrolysates. They found that heating at relatively low temperatures (270 C) leads to alkylation of VO^{2+}-P, whereas heating at higher temperatures (370 C) causes dealkylation of these porphyrins.

Finally, despite much research into the nature of V complexes in crude oils, only VO^{2+}-P have been
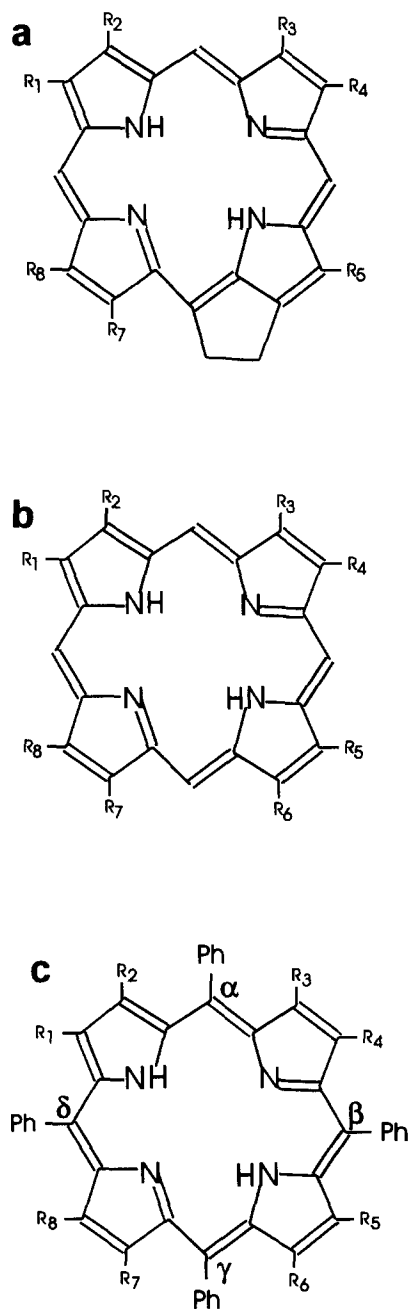

Fig. 1. Generalized structures of: (a) DPEP, (b) ETIO and (c) TPP porphyrins (R$_{1-8}$ = H or alkyl substituents, and Ph = phenyl group).

Table 1. Compositions of organic fractions (%) and the VO^{2+}-P distribution (%) in various organic fractions of LLM and Se sediments and DS asphalt

		Whole organic fraction	Bitumen			Kerogen
			Methanol soluble	Resins	Asphaltenes	
LLM	Organic matter	100	27	8	14	51
	VO^{2+}-P	100	10	1	27	62
Se	Organic matter	100	11	—	3	86
	VO^{2+}-P	100	>1	—	5	>90
DS	Organic matter	100	18	21	61	—
	VO^{2+}-P	100	1	17	82	—

separated and unequivocally identified. The V-non-porphyrins have been characterized by size exclusion chromatography/inductively coupled plasma atomic emission spectrometry (SEC/ICP) (Fish and Komlenić, 1984; Biggs et al., 1985), which indicate that these V complexes cover a range of molecular weights from several hundred to several thousand daltons (D). No such complexes, however, have been isolated and characterized. Recently, Pearson and Green (1993) pointed out that SEC/ICP information concerning the molecular weights of V complexes may be erroneous due to the strong association of porphyrins with asphaltenes.

In view of these experimental data, the thermal stability of VO^{2+}-P incorporated into organic structures of the DS asphalt and the LLM/Se rocks has been investigated with the object of gaining further insight into the organic geochemistry of VO^{2+}-P during the kerogen forming/cracking processes. For this reason, we have conducted laboratory heating experiments to follow the fate of VO^{2+}-P using ESR. Heating experiments have been carried out on the asphaltene/resin fractions of the DS asphalt, the LLM and Se rocks and kerogens. Comparative studies were also conducted with isolated VO^{2+}-DPEP/ETIO, and commercial VO^{2+}-ETIO/-TPP.

EXPERIMENTAL

Samples

The sample of DS asphalt was taken from a large block floating in the north of the lake: it consists of ≥ 99.9% organic matter with an H/C ratio of 1.3.

The LLM limestone and Se marl have approximately 11% and 36% organic matter by weight, respectively. Unheated kerogens gave C (71.5%), H (6.5%), (H/C = 1.1) for the LLM rock and C (61.0%), H (5.5%), (H/C = 1.1) for the Se rock. Although analytical data obtained from outcrop samples make interpretation difficult, we consider that the samples analyzed contain largely Type II kerogen.

Supplementary information is available for the DS asphalt (Nissenbaum, 1978) and the LLM and Se rocks (Premović et al., 1986; Premović, 1987). Commercial VO^{2+} ETIO was purchased from Mid-century (U.S.A.).

Separation and extraction

The DS asphalt was dissolved by refluxing (Soxlet) for 48 h in benzene:methanol (6:1 v/v), centrifuged (2 h) and the supernatant filtered (5 μm pore filter). After solvent evaporation, the asphalt (10 g) was refluxed (Soxlet) for 90 h in methanol to obtain the methanol soluble fraction (after solvent evaporation). The remaining (resin + asphaltene) fractions was refluxed (Soxlet) in n-pentane for 90 h to yield the resin fraction. The remaining asphaltenes were washed several times with n-pentane until the wash solution was clear, then dried at 45°C. All fractions were weighed and examined by ESR/UV-VIS spectrophotometry to determine their VO^{2+}-P content (mainly in the asphaltene fraction) (Table 1).

Bituminous rocks were crushed and extracted with benzene:methanol (6:1 v/v). Carbonates and silicates were removed with HCl/HF, and the pyrite was decomposed with $LiAlH_4$ (Lawlor et al., 1963). The residue was extracted with benzene:methanol (6:1 v/v) and the isolated kerogen was examined by X-ray diffraction.

Sediment extracts were fractionated as above. The VO^{2+}-P distribution in the methanol soluble fraction, resins, asphaltenes and kerogen was determined by ESR/UV-VIS (except kerogen) analyses (Table 1).

Asphaltene (1 g) was dissolved in 80 ml of p-xylene and extracted (×10) with 100 ml aliquots of pyridine/water (4:1 v/v). To prevent reprecipitation of the asphaltenes, about 280 ml p-xylene was added during extraction. The ten extracts were combined, filtered to remove entrapped asphaltenes particles, evaporated (vacuum) and stored in the dark (Fish et al., 1984). This material in 10% methylene chloride:hexane was applied to a silica gel column and eluted with either hexane or hexane:methylene chloride. The eluates were monitored by ESR. Three fractions were obtained: fraction 1, the least polar eluted in hexane; fraction 2, eluted in 30% methylene chloride:hexane; and fraction 3, the most polar eluted in 50% methylene chloride:hexane.

Gel permeation chromatography (GPC) of the LLM/Se asphaltenes was carried out on Sephadex LH-20 (Pharmacia, approximate exclusion limit MW 2000 D), and Styragel 1000 (Waters, approximate exclusion limit MW 30,000 D). The Sephadex column was calibrated using a meso-porphyrin dimethyl ester

and phaeophytin (Blumer and Snyder, 1967). Polystyrene standards were used for MW calibration of the Styragel column. The eluates from the Sephadex/Styragel experiments were combined to give three arbitrary MW fractions: (L) < 4000 D, (M) < 8000 D and (H) < 30,000 D.

Ultraviolet (UV)-visible (VIS) spectrophotometry

UV-VIS spectra were recorded on a Zeiss Specord Model. In general, spectra with maxima occurring at about 409 (Soret), 534 (β) and 573 nm (α) are typical of VO^{2+}-DPEP. Concentrations of extractable VO^{2+}-P were calculated from the UV-VIS spectra, using both the α-peak (573 nm, $\epsilon = 2 \times 10^4$ mol^{-1} cm^{-1}) and Soret peak (409 nm, $\epsilon = 3.3 \times 10^5$ mol^{-1} cm^{-1}) (Hodgson *et al.*, 1967). The presence of VO^{2+}-DPEP was confirmed by observing diagnostic shifts in the Soret band on complexation with piperidine (Baker *et al.*, 1964; Premović *et al.*, 1986).

Electron spin resonance (ESR)

ESR measurements were performed on unheated and heated samples in a quartz tube (4 mm o.d.) using a Bruker ER 200 D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz interfaced to a KORAK computer. The hyperfine coupling constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for which the nitrogen hyperfine splitting (a_N) equals 1.309 ± 0.001 mT (Faber and Fraenkel, 1967). Signal intensities (proportional to the VO^{2+}-P concentration) were calculated by double integration of the first derivative ^{51}V hyperfine (m = $-3/2$) line using the KORAK system. Calculations of the VO^{2+}-P distribution in various fractions were based on comparison with the total organic extract.

Simulated isotropic spectra were calculated using a Fortran program for s = 1/2 systems modified to include I = 7/2. Linewidths of anisotropic/isotropic spectra were measured directly from experimental spectra on an expanded scale (1 cm = 2 G). The ESR spectrum of VO^{2+}-P in the LLM bitumen was recorded at Q-band (35 GHz) with a Varian E-115 spectrometer.

Atomic absorption spectrometry (AAS)

AAS was carried out on a Perkin–Elmer model 360 AA spectrophotometer with a UDR-3 digital read out-unit. A nitrous oxide/acetylene flame was used. V concentrations were measured at 437.924 nm. For further details see Marinković (1963).

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of organic extracts were obtained using KBr discs, using a Perkin Elmer 1600 FTIR spectrometer.

Isolation of the VO^{2+}-P concentrate

To a column (1 cm i.d. × 30 cm) containing Merck Kieselgel 60 (10 g) the methanol fraction was applied in 3 × 2 ml of toluene:chloroform (3:1): this was eluted at 1 ml min^{-1} with toluene, toluene:chloroform (1:1) and toluene:methanol (9:1). Fractions (1–2 ml) were evaporated in a stream of nitrogen to near dryness, for examination by ESR to determine relative VO^{2+}- content, most of which was eluted in the toluene fraction. This fraction was further purified by preparative thin layer chromatography (TLC) using Merck precoated silica plates and toluene:chloroform (1:1) as eluent. The VO^{2+}-P compounds were recovered from the upper red porphyrin band using benzene:methanol (3:1). The presence of predominant VO^{2+}-DPEP and minor VO^{2+}-ETIO components was confirmed by UV-VIS and by observing diagnostic shifts in the Soret band on complexation with piperidine (Premović *et al.*, 1986).

Heating experiment

Samples (100 mg) were sealed under vacuum in quartz tubes (4 mm o.d. and 3 mm i.d.) after flushing with nitrogen then heated at 300, 400, 500 and 600°C for 1–20 days (see Figs 4–8).

After heating, each tube was broken and the material was weighed and then refluxed with benzene:methanol (6:1 v/v). After 24 h, during which the samples were agitated several times, the non-extractable matter was separated. The mass of the non-extractable fraction was determined by weight loss upon combustion.

RESULTS AND DISCUSSION

ESR spectral properties

The goal of this section of the present work is to discuss further some of the ESR features of VO^{2+} in the asphaltene/kerogen fractions (Table 1) and related materials which strongly support our earlier interpretation (Premović *et al.*, 1986; Premović and Jovanović, 1992).

The general conclusion from previous geochemical studies has been that the source rock of the Boscan crude is LLM (Hedberg, 1931). V-X-ray absorption spectroscopy (V-EXAFS) examination of Boscan crude asphaltenes indicated that only the VO^{2+}-P model compounds fit the structural data (Goulon *et al.*, 1984). Selected VO^{2+}-non-porphyrins did not fit well. Photoelectron spectroscopy of V-containing compounds in the same asphaltenes show energy levels similar to those of N4 coordinated model compounds and VO^{2+}-P (Berthe *et al.*, 1984; Novelli *et al.*, 1984). Finally, a solid-state 34 GHz ESR study of the Boscan crude asphaltenes showed isotropic and anisotropic ESR features characteristic for VO^{2+}-P (Malhotra and Buckmaster, 1985). Recently Huffman *et al.* (1992) found that V-EXAFS of VO^{2+}-TPP is

nearly identical to that of the Boscan crude and its asphaltene fractions indicating that the predominant form of VO^{2+} in these materials is VO^{2+}-P.

Some researchers disagree, however, on the solitary existence of VO^{2+}-P as the VO^{2+} moieties in the Boscan crude/asphaltene structures. Using ESR and HPLC, Reynolds et al. (1987) identified the V compounds obtained by pyridine:water extractions of the Boscan and other crudes. Boscan crude extracts consist predominantly of very small molecular weight V compounds with an average MW 350 D. Briefly, ESR studies showed a moderately polar fraction of the Boscan crude pyridine:water extracts to contain a predominance of non-porphyrin VO^{2+} compounds of the N_2S_2 and NOS_2 types. However, these authors failed to discuss the possibility that pyridine:water might remove various V ions (including VO^{2+}) from the inorganic/organic phases. These ions may combine with pyridine and water and/or extracted inorganic/organic compounds forming non-porphyrin V complexes (including those of VO^{2+} of the N_4, N_2S_2, NOS_2 types): pyridine is known for its high sequestering ability for metal (including V) ions (Selbin, 1965; Moore and Dunning, 1955). The MW of the most common four-coordinate (square-pyramidal) VO^{2+}-pyridine complex ion is about 373 D which is consistent with such a possibility. VO^{2+}-P may also form mixed complexes with pyridine (Newton and Davis, 1975) present in the pyridine:water extracts of the heavy crude investigated. In addition, VO^{2+}-P are capable of association as dimers or polymers (Blumer and Rudrum, 1970; Dickson and Petrakis, 1970; Hambright, 1975; Subramanian, 1975). Thus, further work is needed to

establish the origin and nature of VO^{2+} complexes present in the crude pyridine:water extract. We examined pyridine:water extracts of the DS, LLM and Se asphaltenes for V by AAS. The V concentration of these extracts varies between 3% (DS) to 5% (Se) of total asphaltene V. However, no VO^{2+} compounds in either the pyridine:water extracts or their subfractions were detected by ESR.

Wüthrich (1965) showed that for some VO^{2+} complexes, the isotropic coupling constant a_0 reflects the average equatorial ligand environment of the VO^{2+} ion. For square-pyramidal complexes of VO^{2+} the experimental a_0 can be predicted by the additivity relationship $a_0(calc) = \Sigma a_{0,i4}$ where i sums over the different types of equatorial ligand functionalities; a_0 is the experimental isotropic coupling constant for a VO^{2+} complex having all four groups the same; and, n_i is the number of ligand-donor groups (such as N, S, and O) in the equatorial plane.

The isotropic (room-temperature) ESR spectrum of VO^{2+}-P (in benzene) in the Se asphaltenes is shown in Fig. 2. Similar spectra were recorded for the fractions noted in Table 1. In general, these spectra consist of the 8-line ^{51}V hyperfine structure being resolved. The isotropic ESR parameters are $g_0 = 1.984 \pm 0.005$ and $a_0 = 9.5 \pm 0.2$ mT. These parameters are identical (within experimental error) for VO^{2+}-DPEP, synthetic VO^{2+}-TPP and (extracted/commercial) VO^{2+}-ETIO-P. Using the additivity calculation of Wüthrich (1965), Chasteen (1980) estimated that a_0 (calc) for the VO^{2+} complexes with N_2S coordination should range between 8.2 to 8.6 mT, lower than the measured (9.5 mT). Even if these compounds with $a_0 = 8.2-$
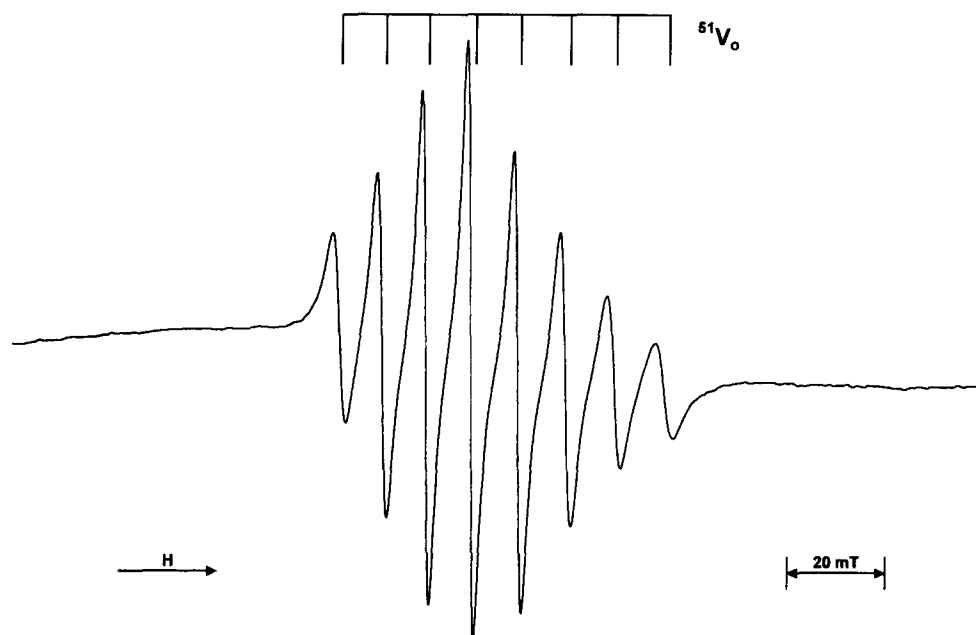

Fig. 2. First derivative room temperature, X-band isotropic ESR spectrum of VO^{2+}-P of the Se asphaltenes.
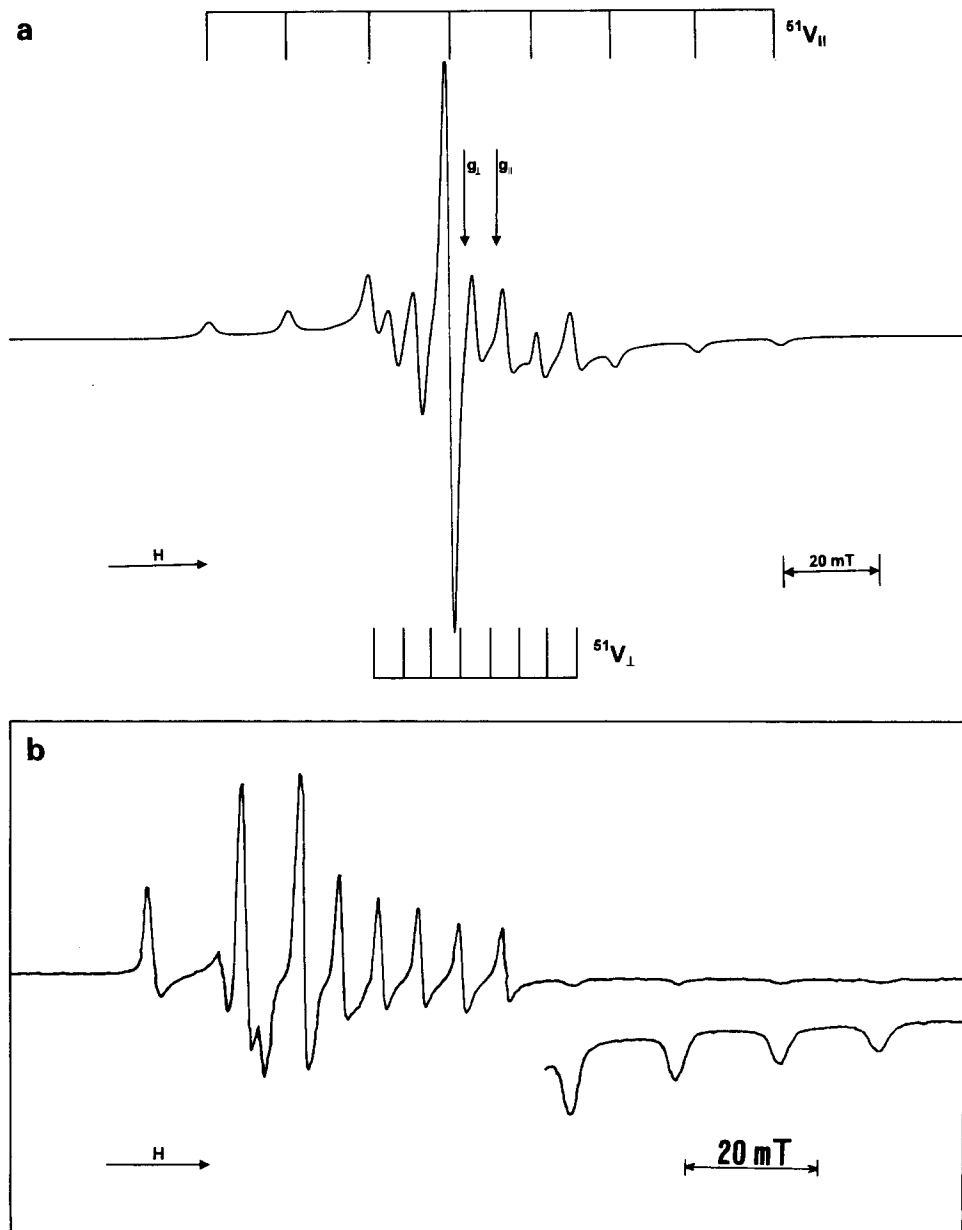
Fig. 3. First derivative room temperature: (a) X-band anisotropic ESR spectrum of VO^{2+}-P of the Se asphaltene (ESR parameters: $A_\parallel$ = 17.6 ± 0.2 mT, and $A_\perp$ = 5.7 ± 0.4 mT) and, (b) Q-band anisotropic ESR spectrum of VO^{2+}-P of the LLM bitumen.

8.6 mT were present at 100 times lower concentration they would have been readily detected by the ESR instrument used.

Anisotropic ESR spectra of the asphaltene/kerogen fractions of LLM, Se, and DS were similar to that of the Se asphaltenes (Fig. 3a). In general, these spectra gave a 16-line anisotropic pattern, due to interaction of the ^{51}V nucleus with its unpaired electron, and displayed parallel and perpendicular features characteristic of polycrystalline (amorphous) samples. Therefore, the VO^{2+}-P sites in the asphaltene/kerogen structures have the same ESR parameters since

there is only one set of lines in their spectra. Also, the absence of any small splitting of the perpendicular components of the spectra implies that these sites have axial symmetry, aside from any possible rhombic distortions much smaller than the linewidth of 1.0 mT.

Experimental ESR parameters ($A_\parallel$ and $A_\perp$) for VO^{2+}-P in the Se asphaltene fraction, derived from their anisotropic ESR spectrum (Fig. 3a), are in good agreement with previously published values for: VO^{2+}-ETIO (O'Reilly, 1958, 1959; Graham, 1987); VO^{2+}-porphin (Bohandy *et al.*, 1974); the coal

VO^{2+}-P (Hocking and Premović, 1978); VO^{2+}-P in the Circle Cliffs and Boscan asphaltenes (Graham, 1987); and identical for VO^{2+}-P incorporated into the LLM and Se kerogens. In addition, VO^{2+}-DPEP extracted from organic fractions of the LLM and Se carbonaceous rocks and DS asphalt (Table 1) and commercial VO^{2+}-ETIO (dissolved in a high-viscosity oil) have identical anisotropic ESR spectra to that of anisotropic VO^{2+}-P in the Se asphaltenes Fig. 3a).

The extension of the Wüthrich relationship by Holyk (1979) to A values has proved useful in studies of VO^{2+} complexes. In fact, A (calc) and a_0 (calc) are in agreement with their experimental counterparts. A (calc) and A (exp) are generally within 0.5 mT. Simple calculations, using the additivity relationship for A_i (calc) and the A_j (exp) hyperfine coupling constants for a number of the VO^{2+} complexes with N_4/S_4 coordination selected by Holyk (1979), indicate that VO^{2+} in an N_2S_2 coordination should show a rhombic distortion between 2.3–4.1 mT, much higher than the observed linewidth of about 1.0 mT.

Often X-band spectra can be described by axially symmetric ESR parameters. However, at the Q-band frequency (35 GHz), the presence of symmetry lower than axial becomes evident for many VO^{2+} compounds (e.g. VO^{2+} complexes with the N_2S_2 first coordination). This is due to the fourfold increase in magnetic field resolution of g-tensor components at the higher frequency. For this reason, we recorded a Q-band anisotropic ESR spectrum of VO^{2+}-P of the LLM bitumen (Fig. 3b). Within 1.0 mT resolution this spectrum is axial, supporting our earlier contention that VO^{2+}-P are the predominant form of VO^{2+} in the LLM bitumen (Premović et al., 1986).

According to Reynolds et al. (1987) the moderately polar fraction of the Boscan crude has isotropic g_0/a_0 ESR parameters indicating the N_2S_2 first coordination around a VO^{2+} ion instead of N_4 as expected for VO^{2+}-P. Their suggestion is based on the differences of these parameters for VO^{2+} in this fraction and the VO^{2+}-P model (ETIO/octaethyl) compounds (Table 2). Reynolds et al. (1987) reported g_0-values as 1.9798 (octaethyl) and 1.9801 (Boscan): the difference in Δg_0 of 0.0003, is well below expected minimum experimental uncertainty in the g_0-measurement (0.001) for the VO^{2+} complexes in liquid solution (Table 2). In fact, the g_0/a_0 ESR

parameters for VO^{2+} in the moderately polar fraction of the Boscan and the VO^{2+}-P model compounds are so close (Table 2) that we suggest, with confidence, that this Boscan fraction contains predominantly VO^{2+}-P.

Sundararaman et al. (1988) pyrolyzed different molecular size fractions of asphaltenes isolated from VO^{2+}-P rich Boscan crude and demonstrated that the VO^{2+}-ETIO are preferentially associated with the asphaltene/kerogen fractions. According to these authors there are three V-containing components in the Boscan asphaltenes. One corresponds to free VO^{2+}-P isolable by standard procedures (Sundararaman, 1985); the other two correspond to larger molecular size fractions described as "non-porphyrin V" by Biggs et al. (1985). Sundararaman et al. (1988) concluded that VO^{2+}-ETIO are bound in, or to, the large molecular size fractions of asphaltenes.

The three (L, M and H) fractions of the LLM and Se asphaltenes separated by preparative GPC had isotropic ESR spectra similar to fraction H of the Se asphaltenes, which is, in turn, identical to the isotropic VO^{2+}-P spectrum of the Se asphaltenes (Fig. 2). In accordance with Sundararaman et al. (1988), fraction H of the asphaltenes contained "free" VO^{2+}-P, showing strong absorptions at ca. 550 and 570 nm which were absent in fractions L and M.

For this reason VO^{2+}-P will also include these (minor) VO^{2+}-N_4 compounds with modified porphin structure which are derived from these metal-P. They, in many cases, lose some of their basic porphin properties (e.g. Soret UV and characteristic VIS bands) but keep others (e.g. the ESR spectrum similar to that of VO^{2+}-P, Fig. 2).

Pyrolysis of the asphaltene/kerogen VO^{2+}-P

Table 1 shows the distribution of VO^{2+}-P in sub-fractions separated from the DS asphalt, and from the LLM and Se sediment extracts and kerogen. Asphaltenes from the asphalt contain the highest concentration of VO^{2+}-P, while the kerogen fraction of the sediments accounts for the major part of VO^{2+}-P. The kerogen VO^{2+}-P are, in fact, the most characteristic property of these rocks (Premović et al., 1986). The LLM and SE kerogens, and the DS asphaltene spectra (not shown) were identical to the ESR spectrum of the SE asphaltenes (Fig. 3a).

Table 2. Isotropic g_0/a_0 ESR parameters of the VO^{2+}-P model compounds and the Boscan moderately polar fraction*

VO^{2+} system	g_0	a[mT]	Δg_0† [± 0.001]‡	Δa_0† [± 0.05 T]‡
etio	1.9788	9.520	0.0013	0.04
octaethyl	1.9798	9.508	0.0003	0.052
Boscan	1.9801	9.560	—	—

*According to Reynolds et al. (1987).
†The difference between the corresponding ESR parameters for the Boscan fraction and the VO^{2+}-P model compound.
‡Expected minimum uncertainty of the measurement of the g_0/a_0 ESR parameters employing a proton resonance gaussmeter for the magnetic field calibration. DPPH ($g_0 = 2.0036 \pm 0.0001$) as frequency marker and a computer simulation (Holyk, 1979).
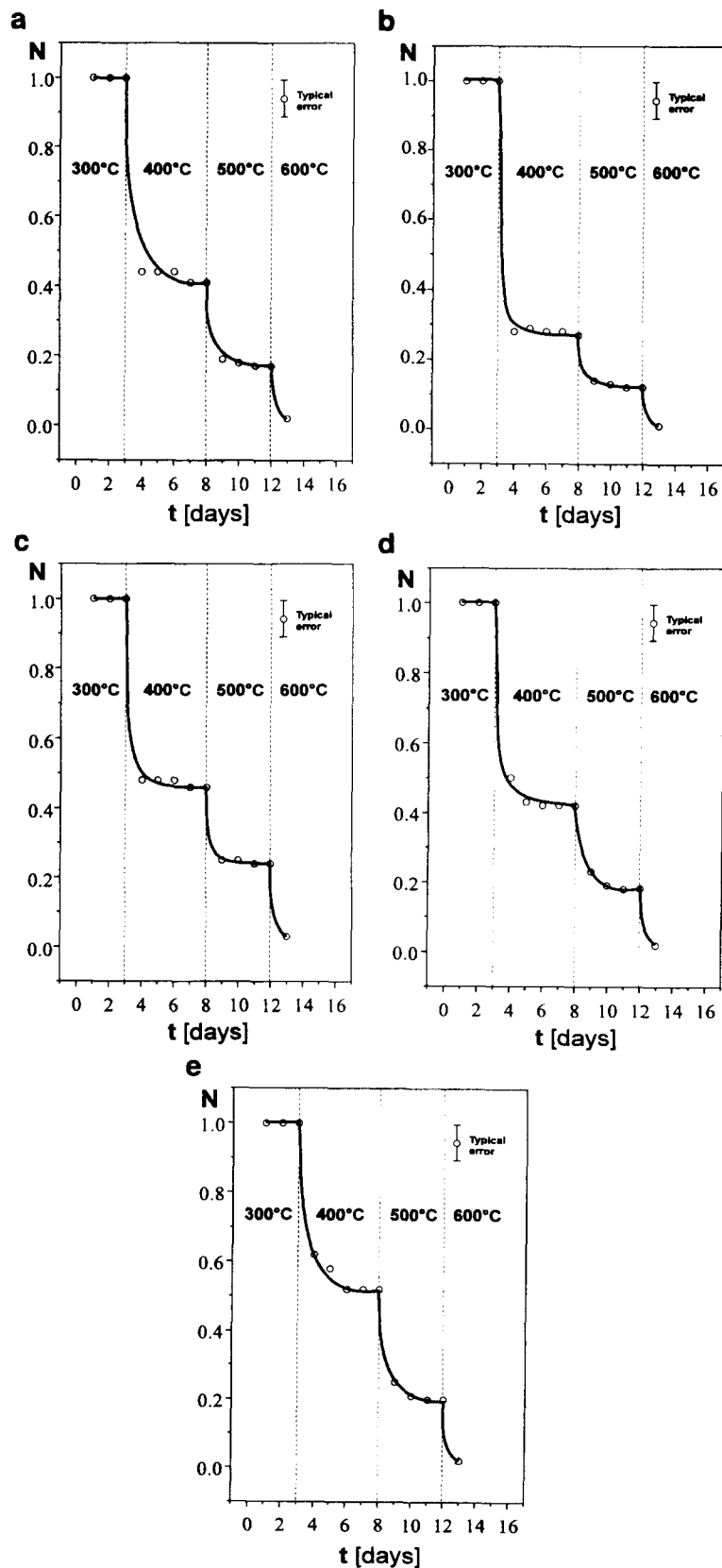
Fig. 4. Decrease in normalized ESR signal intensity N of VO^{2+}-P as a function of time, the temperature changes being from 100 C to 600 C (at 100 C intervals) during laboratory pyrolysis of: (a) the DS asphaltenes, (b) resins and (c) asphalt; and, (d) the LLM and (e) Se asphaltenes.

Figure 4a shows changes in the relative ESR signal intensity (N, normalized to the signal intensity of the unheated DS asphaltene) of VO^{2+}-P as a function of pyrolysis temperature and time. As this intensity is directly proportional to the VO^{2+}-P concentration, we deduce that the VO^{2+}-P content changes dramatically over the temperature range studied. Up to about 300°C, no change (within experimental error) occurs, but above this about 30% of the total DS asphaltene is converted into DS pyrobitumen. During the first stages of heating at 400°C (ca. 5 days) > 95% of the DS asphaltenes is transformed into the DS pyrobitumen, also the VO^{2+}-P content decreases sharply and then remains relatively constant with increasing time. At 500°C and 600°C, the VO^{2+}-P content change per temperature or time unit was similar to that at 400°C, except that at 600°C it was reduced in less than 1 day to < 10 ppm, the limit of ESR detection for VO^{2+}-P. Temperature effects on VO^{2+}-P of the DS resins and asphalt are shown in Fig. 4b,c, respectively. As expected, the thermal changes in the DS asphaltenes (Fig. 4a) and resins (Fig. 4b) VO^{2+}-P (99% of total VO^{2+}-P, Table 1) are similar to that of the asphalt (Fig. 4c).

Finally, we found that the VO^{2+}-P kinetic patterns for the LLM (Fig. 4d) and Se (Fig. 4e) asphaltenes resemble those for the DS asphaltenes (Fig. 4a) and resins (Fig. 4b). In addition, the thermal conversion of these two materials into the kerogen-like material is, also, comparable to the DS asphaltenes (Premović et al., 1995).

Pyrolysis of LLM and Se kerogen VO^{2+}-P (Fig. 5) gave qualitatively similar results to that of the DS (Fig. 4a), LLM (Fig. 4d) and Se (Fig. 4e) asphaltenes VO^{2+}-P, although they differ quantitatively. No

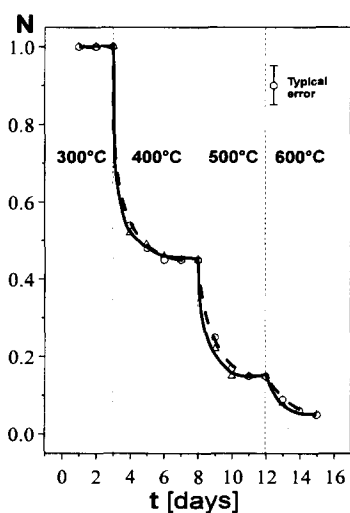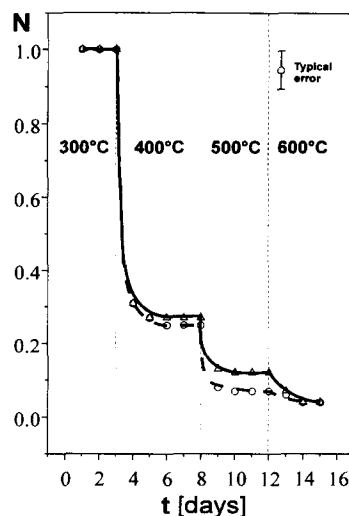Fig. 6. Decrease in normalized ESR signal intensity N of the kerogen VO^{2+}-P as a function of time, the temperature changes being from 100°C to 600°C (at 100°C intervals) during laboratory pyrolysis of carbonate-free samples: the LLM limestone (——△——) and Se marl (—O—).

difference was observed between the two kerogens throughout the entire temperature range (Fig. 5). It is worth noting that little change in the VO^{2+}-P content of the LLM kerogen occurs before the onset of significant hydrocarbon generation (T_{max}429°C, Talukdar et al., 1986).

FTIR indicates that the 1360–1380, 1460, 2850 and 2920 cm^{-1} aliphatic bands are stable in these materials during heating in vacuum to ca. 300°C although the spectra show a loss of oxygen associated with diminution of the C = O band at ca. 1750 cm^{-1} (Robin, 1975). At this temperature the kerogen weight loss was less than 3%. At 400°C aliphatic bands decreased markedly, whereas C = C peaks in aromatic moieties increased. At this temperature, the kerogen weight loss was < 10%, and the H/C ratio decreased to ca. 0.9. Similar changes in the FTIR spectrum and the H/C ratio were observed for both the DS kerogen and asphaltenes at up to 300°C.

According to Tissot and Welte (1984), heating kerogen to ca. 350°C (late diagenesis stage in sedimentary basins) results in a rupture of heteroatomic bonds, generating small units containing one to several nuclei and aliphatic chains. Heating at ca. 350°C to 500°C (catagenesis stage) results in cleavage of stronger bonds. This agrees with our observations of a decrease in aliphatic absorptions in the FTIR spectra and H/C ratios of the kerogens, in agreement with the findings of Robin (1975). Our results suggest that even in sedimentary rocks with mature kerogens a minor amount of soluble VO^{2+}-P (alkyl type and associated with the asphaltene and resin structures) will have originated from thermal cracking of the kerogen. It is possible that the catalytic activity of clay minerals may influence the

Fig. 5. Decrease in normalized ESR signal intensity N of VO^{2+}-P as a function of time, the temperature changes being from 100°C to 600°C (at 100°C intervals) during laboratory pyrolysis of: the LLM (——△——) and Se (—O—) kerogens.

thermal decomposition of the kerogen VO^{2+}-P under laboratory as well as natural conditions. Therefore we have pyrolyzed kerogens in the LLM and Se carbonate-free sediment samples as for their isolated kerogens. However, the VO^{2+}-P kinetic patterns for the carbonate-free samples (Fig. 6) are similar to those for isolated kerogens (Fig. 5). This result suggests that the clay minerals in the rocks have little or no effect on the kerogen VO^{2+}-P pyrolytic decay.

Finally, a very rapid decrease in the concentration of VO^{2+}-P in the kerogen/asphaltene fractions at ca. 400 C and above emphasizes that precautions must be taken when interpreting changes in VO^{2+}-P during simulated maturation experiments at temperatures above 300 C.

Pyrolysis of VO^{2+}-DPEP, ETIO and TPP

The content of VO^{2+}-DPEP (Fig. 7) decreased sharply to < 10% of its initial value after about 4 days of heating using the conditions outlined in the previous section. Similar results were obtained for other alkyl VO^{2+}-P (e.g. for both extracted and commercial ETIO-type). Also, part of the VO^{2+}-DPEP may be converted into VO^{2+}-ETIO at temperatures ≥ 300 C after 4 days of laboratory heating (Didyk *et al.*, 1975; Barwise and Roberts, 1984).

In order to better understand the nature of VO^{2+}-P structures and the reactions involved in their thermal breakdown, a detailed pyrolysis study was made on synthetic VO^{2+}-TPP using the pyrolysis conditions outlined above. At 500 C, the content of VO^{2+}-TPP decreased abruptly to less than 2% of its initial value after about 4 days at this temperature (Fig. 8). The greater stability of VO^{2+}-TPP over the alkyl VO^{2+}-P (Fig. 7) can be rationalized by their structural

Fig. 8. Decrease in normalized ESR signal intensity N of VO^{2+}-TPP as a function of time, the temperature changes being from 100 C to 600 C (at 100 C intervals) during laboratory pyrolysis.

differences. In VO^{2+}-TPP the methine bridge carbons (meso positions: label α-δ, Fig. 1) have phenyl substituents (Hamor *et al.*, 1964), whereas alkyl VO^{2+}-P have no substitution at the methine bridge carbons (Baker and Louda, 1986).

The fact that most of the asphaltenes/kerogen VO^{2+}-P (≥ 60% Figs 4 and 5) are stable up to 400 C infers that alkyl VO^{2+}-P are major constituents of the asphaltenes/kerogen VO^{2+}-P. On the other hand, there is also a significant amount (≤ 50%) of the asphaltene/kerogen VO^{2+}-P, which are thermally resistant at temperatures > 400 C. The high proportion of these relatively thermostable VO^{2+}-P may arise through conversion of alkyl VO^{2+}-P (incorporated into the asphaltene/kerogen matrix) during either diagenetic/catagenetic processes or laboratory heating. The data presented here are, however, not sufficient in themselves to provide a clear cut decision between these two possible options.

Step-wise kinetic pattern

The disappearance of VO^{2+}-P in the asphaltene/kerogen structures follows step-wise kinetics (Figs 4 and 5). A general characteristic of such a process is that above a certain temperature the number of species first decreases relatively fast at a fixed temperature, then tends toward a constant value. When the temperature is increased, the process repeats itself, until the final temperature is reached, when all active species disappear. The step-wise processes were interpreted as corresponding to events having certain activation free energy distributions (Hedvig, 1975). The fact that the MW of VO^{2+}-P of the asphaltenes ranges from < 400 D to < 30,000 D supports this conclusion. This is further supported by an earlier contention of Blumer (1974) who estimated
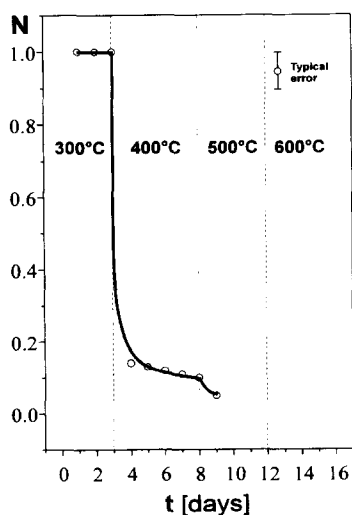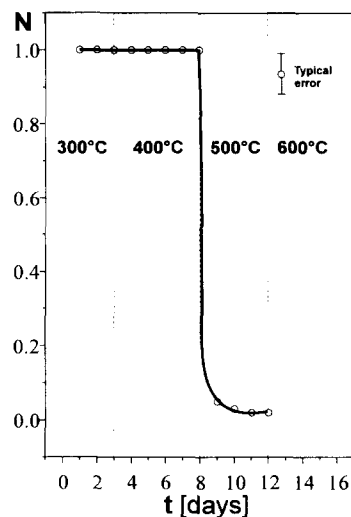

Fig. 7. Decrease in normalized ESR signal intensity N of VO^{2+}-DPEP/ETIO concentrate as a function of time, the temperature changes being from 100 C to 600 C (at 100 C intervals) during laboratory pyrolysis.

that more than 2×10^6 chemically distinct porphyrins (mostly VO^{2+}-P) are present in the bitumen fraction of the Se marl. In addition, the presence of VO^{2+}-P in the Boscan asphaltenes with MW ranging from < 900 D up to > 9000 D (Fish and Komlenić, 1984; Fish *et al.*, 1984) is in line with this notion indicating that the reactions with higher and higher energies are occurring with increasing temperature. However, a small amount of VO^{2+}-P (< 5% of initial VO^{2+}-P content) remains even after prolonged heating at 600°C suggesting that total loss is done to very high activation energies.

Under the pyrolysis conditions used it is possible that the porphyrin rings of VO^{2+}-P are hydrogenated, which, if sufficient, will be susceptible to demetalation/decomposition (Hodgson, 1973; Fish *et al.*, 1984). This may represent the mechanism by which VO^{2+}-P is demetalated/decomposed in our work. Hence, the distribution of activation energies, described above, for the asphaltenes/kerogen VO^{2+}-P studied can be understood if one assumes that (at least up to 500°C) the process of demetalation/decomposition occurs through free-radical intermediates. In fact, free-radical reactions in solid systems are characterized by step-wise kinetics (Hedvig, 1975). An investigation to further clarify this problem is in progress.

Static laboratory pyrolysis and catagenesis

The present experiments are in line with the claim that laboratory and geothermal (due to burial) heating of kerogen may not be equivalent. For example, according to our data the disappearance of kerogen's alkyl VO^{2+}-P at 400°C approximates a first order reaction with a half-life of about 1 day. If half of this reaction is complete in 1 day at 400°C or ca. 3 yr at 300°C, then, assuming the Arrhenius equation holds, half the reaction will also be complete in around 100 yr at 250°C or in 10^{11} yr at 100°C. Between 400°C and 300°C, the often-quoted result of a doubling of reaction rate for each 10°C rise in temperature is applicable, but between 250°C and 100°C each 5°C change alters the rate by a factor of two. According to current pedagogy, crude is produced from kerogen (during catagenesis) at approximately 50°C and 150°C: the "principal zone of oil formation" (Vassoevich *et al.*, 1974) which lies within the above interval.

If the average temperature for petroleum generation from kerogen (such as the LLM material) can be set at around 100°C and assuming that 10 half-lives will reduce the concentration below detectable limits, then at 100°C, alkyl VO^{2+}-P would have been decomposed/converted in 10^{12} yr which is roughly 200 × the age of Earth. Our extrapolations (of present results to longer times) can do little more than suggest orders of magnitude, but clearly show that the use of static laboratory pyrolysis of kerogen does not realistically simulate geological processes of this material (Waples, 1984).

Electronic structure of the asphaltene/kerogen VO^{2+}-P

Blumer and Snyder (1967) studied high molecular weight VO^{2+}-P in the Se marl and presented evidence for the existence of a homologous series of asphaltenes VO^{2+}-P extending to MW of ca. 20,000 D. ESR spectral parameters for the asphaltenes/kerogen VO^{2+}-P are not different from those of alkyl VO^{2+}-P. This suggests that the incorporation of alkyl VO^{2+}-P into either the asphaltene/kerogen structures has not affected such fine detail of electronic structure as the distribution of unpaired d-electron density of VO^{2+} in the VO^{2+}-P conjugated ring system. Blumer and Snyder (1967) pointed out that the 20,000 D asphaltenes VO^{2+}-P fraction represents only a minor part of the total asphaltenes VO^{2+}-P and reasoned that VO^{2+}-P in the high molecular weight fraction of the Se asphaltenes is mainly associated with much larger polymer systems (ca. 30,000–50,000 D).

Anaerobic kerogenization of asphaltenes

Pyrolysis of deaerated asphaltenes, isolated from the DS asphalt, produced an insoluble product which had a similar content of VO^{2+}-P as the initial asphaltenes. Initial results indicated that temperatures below about 150°C were insufficient to cause an appreciable reaction within reasonable time. Consequently, this part of the study was carried out at temperatures of 150, 200 and 250°C (Fig. 9). Both atomic H/C (= 1.4) and O/C (= 0.05) ratios for the insoluble material produced during this heating indicate that it was similar to natural kerogen. Similar results were obtained for the DS asphalt and LLM/Se asphaltenes. The fact that this insoluble product had not been previously found is not surprising. Most previous research on the thermal behavior of sedimentary VO^{2+}-P was concerned with the relative proportions of VO^{2+}-DPEP and VO^{2+}-ETIO which is used as an indicator of thermal maturity (Sundararaman, 1993).
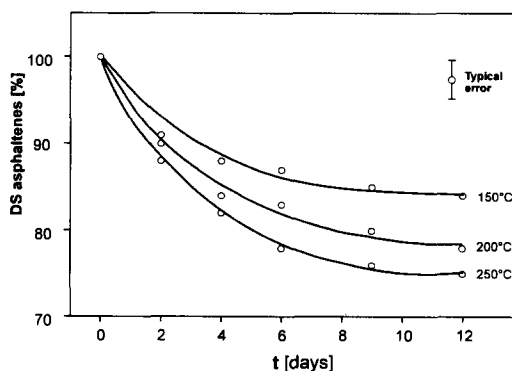

Fig. 9. The amount of the DS asphaltene (%) remaining on heating at 150, 200 and 250 C for 1–12 days in the absence of air.

The results shown in Fig. 9 indicate that VO^{2+}-P are incorporated into kerogen-like material under mild thermal conditions ($< 200°C$). This implies that a significant amount of the VO^{2+}-P which were not incorporated into the kerogen precursor/ young kerogen during diagenesis could be incorporated into a secondary kerogen (asphaltene-derived kerogen) in deeper sedimentary layers either before or during the petroleum generation stage (catagenesis).

Origin of asphaltenes/kerogen and their VO^{2+}-P

Our results support the view that kerogens and asphaltenes contain similar compositional macromolecular structures and consequently, these structures (such as those containing VO^{2+}-P) should follow a similar evolution path during either natural or laboratory heating.

Geochemists generally accept that the formation of the kerogen is the result of either a series of consecutive/random repolymerization and polycondensation reactions of a very small fraction of the bio(degradation) products of extant biomaterials (Tissot and Welte, 1984) or the accumulation of selectively preserved resistant biomacromolecules (Tegelaar et al., 1989). According to the first concept, alkyl VO^{2+}-P units have been incorporated already into the asphaltene/kerogen precursor structures, whereas, according to the second view, the asphaltene/kerogen VO^{2+}-P are associated with macromolecular structures which were highly resistant to degradation.

Very recently, Premović et al. (1995) demonstrated that material with some of the characteristics of kerogen could be generated at lower temperatures ($\leq 100°C$) by the kerogenization of asphaltenes in the presence of oxygen. We suggest that this process may be widespread in petroliferous (especially carbonate) deposits. According to this approach, the asphaltene materials (enriched already in alkyl VO^{2+}-P) are converted into kerogen (rich also in alkyl VO^{2+}-P) during natural heating at temperatures $\leq 100°C$ in the presence of air O_2.

CONCLUSIONS

From the data presented in this work the following conclusions can be reached:

1. The content of the asphaltene/kerogen VO^{2+}-P decreases rapidly during laboratory pyrolysis at temperatures $\geq 400°C$. These changes follow stepwise kinetics.

2. Most of the asphaltene/kerogen VO^{2+}-P are of alkyl-type and are incorporated into the asphaltene/ kerogen structures.

3. Extrapolation of the present results to longer times infers that laboratory simulation of catagenesis is irrelevant to natural reactions which characterize this stage of petroleum genesis.

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