Air oxidation of the kerogen/asphaltene vanadyl porphyrins: an electron spin resonance study

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The thermal behavior of vanadyl porphyrins was studied by electron spin resonance during heating of kerogens, isolated from the La Luna (Venezuela) and Serpiano (Switzerland) bituminous rocks, at 250 ºC for 1 to 20 days in the presence of air. During the thermal treatment of the kerogens, the vanadyl porphyrins resonance signals decrease monotonically and become quite small after 6 days of heating. Concomitantly, new vanadyl signals appear and, at longer heating times, dominate the spectrum. It is suggested that the secondary vanadyl species must have been formed from vanadyl porphyrins. Similar conversions of vanadyl porphyrins are observed under the same experimental conditions for asphaltenes extracted from the La Luna and Serpiano rocks, and floating asphalt from the Dead Sea (Israel). A comparison of the spin-Hamiltonian parameters for vanadyl porphyrins and the vanadyl compounds obtained during pyrolysis of the kerogens/asphaltenes suggests that the latter are of a non-porphyrin type. For comparison a study was conducted on Western Kentucky No. 9 coal enriched with vanadium (>400 ppm) from six mines. All the coal samples show only the presence of predominant by non-porphyrin vanadyl compounds, similar to those generated through laboratory heating of the kerogens/asphaltenes in air. In addition, some samples also contain a minor amount of vanadyl porphyrins.

Keywords: vanadyl porphyrins, kerogen, asphaltene, incorporation, electron spin resonance.

The discovery of electron spin resonance (ESR) signals of vanadyl porphyrins (VO^{2+}-P) in petroleums and asphaltenes by O'Reilly[1] prompted researches to apply the technique for the detection and approximate quantification of low concentrations of VO^{2+}-P in various carbonaceous geological materials with or without resourse to extraction.[2] Hocking and Premović[3] used this technique to study for the first time VO^{2+}-P in the coal/coal-like inclusions of the Athabasca tar sand. Premović[4] and Premović *et al.*[5] applied ESR to estimate the distribution of VO^{2+}-P in the bitumen and kerogen fractions of ancient shaly-type sediments: the La Luna (LL) limestone and Serpiano (Se) marl. Finally, Nissenbaum *et al.*[6] detected VO^{2+}-P in Dead Sea (DS) floating asphalt by ESR.

The purpose of the present work was to carry out an ESR investigation of VO^{2+}-P associated with the kerogens/asphaltenes isolated from the LL and Se rocks before and after laboratory pyrolysis at 250 °C in the presence of air. In addition, VO^{2+}-P in asphaltenes extracted from the DS asphalt float, as well as solid bitumens (imponite/grahamite) from Oklahoma (USA) were also examined. It was expected that these studies might yield additional information about the thermal stability of VO^{2+}-P associated with the kerogens/asphaltenes in the presence of air O_2.[7–9]

EXPERIMENTAL

Sample

The LL and Se rocks have apparently experienced a fairly low temperature history.[5, 10, 11] The most intriguing characteristics of the kerogens isolated from the LL and Se materials is their high VO^{2+}-P content: 4700 ppm (LL) and 2500 ppm (Se).[5,12]

The most spectacular occurrences of bitumen in the DS Basin (Israel) are the huge floating blocks of asphalt on the surface of the DS. The samples of the DS asphalt float (studied in this communication) are of extreme purity (99.9% of extractable organic matter) and are rich in both vanadium (V) (up to 1500 ppm) and VO^{2+}-P (up to 1000 ppm).[12,13]

Asphaltite (grahamite) and asphaltic pyrobitumen (imponite) deposits are found at a number of localities in the Ouachita Mountains (Oklahoma); the best known occurrences are in the Page and Windingstair locations, in southern Le Flore County.[14] Grahamite is partly soluble in common organic solvents and imponite is almost insoluble.[15]

The W. Kentucky (Springfield) No. 9 coal of the Carbondale Formation (Middle Pennsylvanian) in the W. Kentucky coalfield of the Illinois Basin is the most abundant coal in the W. Kentucky coalfield. Very recently, Premović *et al.*[16] applied ESR spectroscopy to probe the chemical and structural environment of the VO^{2+} in the coal/shale samples from the Providence mine (the Union County) of this coalfield enriched with V (>1000 ppm). According to these authors, the coal metal exists as VO^{2+} in which it is bound to oxygen atoms but with no evidence for VO^{2+} as VO^{2+}-P. The coal samples used in the present study came from the top £ 20 mm of the W. Kentucky seam from three mines (Providence, Millport and Nebo) containing up to 800 ppm of V. Parts of the seam are exceptionally rich in V, up to 1800 ppm.[16]

Sample preparation and pyrolysis

The geological samples were ground to a fine powder (200– 400 mesh) with a ball mill and Soxlet extracted exhaustively with benzene/methanol azeotrope to remove soluble organic material (bitumen). The bitumen fraction was dissolved by refluxing (Soxlet) for 48 h in benzene: methanol (6:1 v/v), centrifuged (2 h) and the supernatant filtered (5 mm pore filter). After solvent evaporation, the bitumen (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*-hexane for 90 h to yield the resin fraction. The remaining asphaltenes were washed several times with *n*-hexane until the wash solution was clear, then dried at 45 °C.

The extracted LL/Se rocks were treated with 20% hydrochloric acid (HCl) to remove carbonates. After filtration and washing, the remaining minerals were acid leached by digestion for 72 h at room temperature using a 1:1 by volume mixture of concentrated hydrofluoric acid (HF): 48% and HCl: 20%. The mixture was filtered and the residue washed successively with boiling distilled water to pH 7. After drying, the kerogen concentrate was again exhaustively extracted with benzene/methanol azeotrope until the solvent siphoning to the flask was clear. The kerogen was dried at 80 °C and stored in a desiccator. An identical procedure was employed to obtain the coal insoluble organic fraction. The kerogen/asphaltenes were then heated at temperatures £ 250 °C in air for periods of time between 1 and 20 days.

Electron spin resonance

ESR measurements were performed on the finely-ground powders of the kerogen/asphaltene samples in an ESR quartz tube. The spectra were recorded on a Bruker ER-200 series ESR spectrometer with either a Bruker ER-044 X-band bridge or a Bruker ER-053 Q-band bridge, using standard 100 kHz field modulation. X-band measurements were made at 9.3 GHz utilizing a rectangular TE cavity, and those of the Q-band using a cylindrical TE cavity.

The g-values and hyperfine coupling constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for wich $g = 2.0055 - 0.0001$ and the nitrogen hyperfine splitting, $a_N = 1.309 - 0.001$ mT.[17] A quartz sample tube taped on the exterior of the sample tube was used for the Fremy's solution (*ca.* 10^{-3} M).

RESULTS AND DISCUSSION

VO^{2+} *and pyrolysis of kerogens/asphaltenes: nature and origin of* VO^{2+} *-non-porphyrins*

A typical ESR spectrum of VO^{2+}-P of LL kerogen before heating is shown in Fig. 1a. The LL kerogen was pyrolyzed at 250 °C in the presence of air for 5 days. The X-band anisotropic ESR spectrum of the VO^{2+} compounds in the pyrolyzed sample of
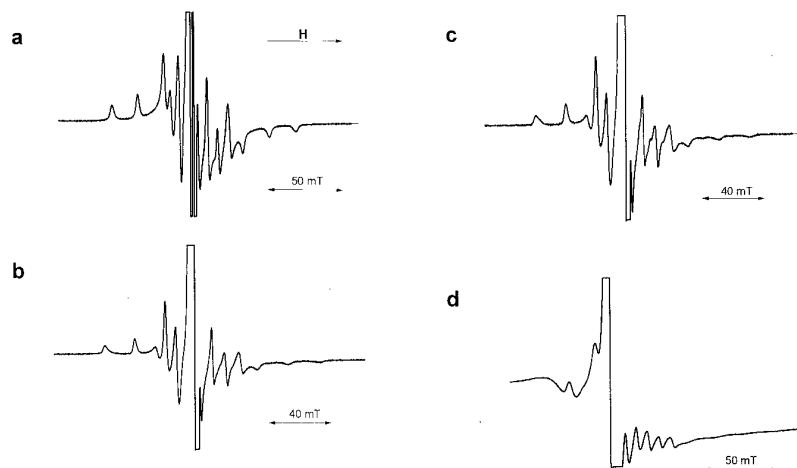

Fig. 1. First derivative, room temperature, X-band ESR spectra of: a) VO^{2+}-P in LL kerogen; b) VO^{2+}-non-P in pyrolyzed LL kerogen; c) VO^{2+}-non-P in the W. Kentucky coal, and d) first derivative, room temperature, Q-band ESR spectrum of VO^{2+}-non-P of pyrolyzed LL kerogen. ESR parameters: $A_{\parallel} = 17.6 - 0.2$ mT, and $A_{\wedge} = 5.7 - 0.4$ mT; $g_{\parallel} = 1.951 - 0.003$ and $g_{\wedge} = 1.985 - 0.010$ (for the VO^{2+}-P^4); $A_{\parallel} = 19.2 - 0.3$ mT, and $A_{\wedge} = 6.9 - 0.5$ mT; $g_{\parallel} = 1.937 - 0.005$ and $g_{\wedge} = 1.991 - 0.010$ (for the VO^{2+}-non-P);

the LL kerogen is shown in Fig. 1b. Similar spectra were recorded for the Se kerogen/asphaltene and the LL/DS asphaltenes after the heat treatment described above.

ESR measurements at 34 GHz have the potential to resolve resonances that might be obscured at 9 GHz and are more sensitive to the g anisotropy. Moreover, 34 GHz measurements are more sensitive to details of the VO^{2+} sites, such as the

presence of symmetry lower than axial. For this reason, the Q-band anisotropic spectrum of the VO^{2+}-species of heated LL kerogen was also recorded, Fig. 1d. Within experimental error (< 1 mT) this spectrum is axial. Hence, in this case, all the spin-Hamiltonian parameters can be derived from this ESR spectrum using the axially symmetric spin-Hamiltonian

$$H = b_0 [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} (S_z I_z) + A_{\perp} (S_x I_x + S_y I_y)]$$

where $g_{\parallel}, g_{\perp}, A_{\parallel}$ and $A_{\perp}$ are the parallel (z) and perpendicular (x, y) components of the g-and ^{51}V hyperfine coupling tensors, respectively. H_i, S_i and I_i represent the vector components of the magnetic field, electron spin, and ^{51}V nuclear spin along the $i(=x, y, z)$ axes, respectively.

A comparison of the spin-Hamiltonian parameters for VO^{2+}-P unheated LL kerogen (Fig. 1a) and heated LL kerogen (Fig. 1b) infers that the VO^{2+} compounds in the thermally treated kerogen are of a non-porphyrin type. In fact, the ESR spectrum of the heated LL kerogen is similar to those reported for the VO^{2+} ions incorporated into the structure of the W. Kentucky coal enriched with V (>1000 ppm) from the Providence mine of the Union county.[16] According to these authors, the VO^{2+} ions within the structure of this coal are, probably, complexed with the oxygenated functional groups (*e.g.*, carboxylic/phenolic groups) of the coal.

Our earlier studies[9,18] demonstrated that the ESR signals given by VO^{2+}-P in the LL/Se kerogens undergo no change on pyrolysis *in vacuo* at temperatures up to 400 °C. This fact indicates that air plays an essential role in the observed conversion of VO^{2+}-P into VO^{2+}-non porphyrins (VO^{2+}-non-P). In separate experiments it was also demonstrated that the active component of air is molecular oxygen (O_2) since pure O_2 at a pressure corresponding to the partial pressure in air was equally effective. Similar experimental results and observations were found for the asphaltenes studied.

The changes of the normalized ESR signal intensity of VO^{2+}-P, VO^{2+}-non-P, and total VO^{2+} in the Se kerogen with heating time can be seen in Fig. 2a. The VO^{2+}-P ESR signals decrease monotonically and become quite small after 6 days of heating. Concomitantly, the VO^{2+}-non-P signals appear and, at longer heating time, dominate the spectrum. Similar VO^+ ESR signal changes are observed during heating of the LL kerogen (not shown). Clearly, the secondary VO^{2+}-non-P signals must have been formed from the principle VO^{2+}-P signals in the ESR spectrum, since the minor VO^{2+} species were not present in sufficient number to account for these large secondary ESR signals.

The VO^{2+}-non-P formed at the expense of the VO^{2+}-P during laboratory pyrolysis of the LL/Se kerogens amounted to *ca.* 80% of the initial VO^{2+} in the VO^{2+}-P, Fig. 2. This fact infers that in this material there are at least, either two different types of incorporated VO^{2+}-P or two different oxygenic degradation pathways of VO^{2+}-P. In both cases, a *less* plausible alternative is that V^{5+} compounds are formed which are "invisible" to ESR. In striking contrast to the kerogens,
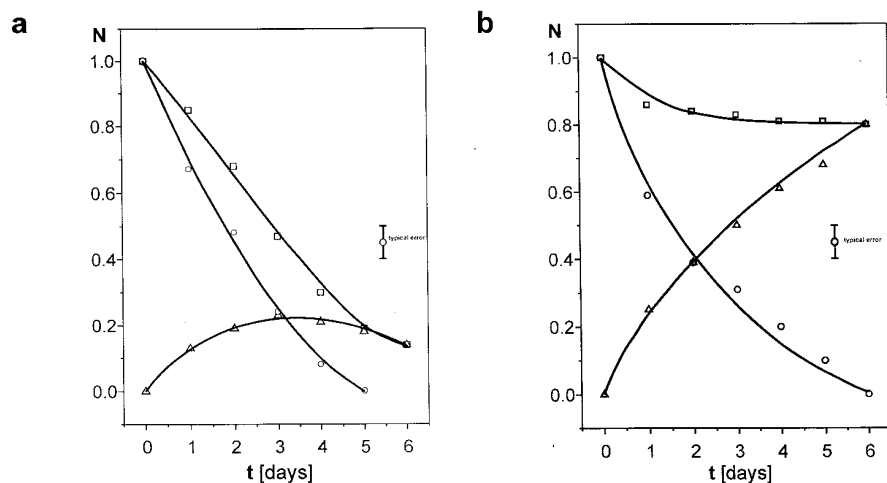
Fig. 2. Changes of the normalized ESR signal intensity (N) for total VO^{2+} ($\square$); VO^{2+}-P (o); and VO^{2+}-non-P(D) for a) the Se kerogen and b) the Se asphaltene.

both the pyrolyzed Se (Fig .2b) and LL (not shown) asphaltenes yield only *ca.* 25% of VO^{2+}-non-P at the expense of the initial VO^{2+}-P. This marked difference in the yield of VO^{2+} as VO^{2+}-non-P (and other pyrolytic features) of these and similar carbonaceous geological materials will be discussed in detail elsewhere. At 250 °C, the VO^{2+}-non-P ESR signals of the LL/Se kerogens diminished after about 20 days of laboratory heating in an air atmosphere.

The thermal conversion of the kerogen/asphaltene VO^{2+}-P into VO^{2+}-non-P could be approximated by first order kinetics at 250 °C with a VO^{2+}-P half-life ($t_{1/2}$) of ~ 2 days. Porphyrins are known to undergo thermal degradation at relatively low temperatures in the presence of air. This process is also known to cause the scission of the porphyrin ring.[19] Consequently, we suggest that the thermal conversion described above occurs through the scission of the porphyrin ring of the VO^{2+}-P, leading to the formation of a hexadentate VO^{2+}-non-P complex containing oxygen ligand donor atoms.

Weathering, which takes place at low temperatures (< 30 °C) is the natural oxidation of kerogen, while oxidation is a higher temperature (>70 °C) event. Natural (mild) oxidation of kerogens, in which the related temperatures do not exceed 150 °C, leads to changes of the original chemical structure with an increase in the content of oxygenated (carbonil carboxylic/phenolic) functional groups. On the other hand, modern studies of the changes in kerogen composition during air oxidation at 200–250 °C have indicated a dramatic increase in the oxygenated (carbonil carboxylic/phenolic) groups, the concentration of which is strictly dependent on the oxidation temperature. According to Kalema and Gavalas,[20] 200 °C oxidation leads to the incorporation of a variety of new oxygen functionalities (carboxylic, carbonyl and phenol units) resulting in the formation of so-called "regenerate humics/protokerogen".

It is generally accepted that the minimum temperature at which irreversible chemical changes of carbonaceous geological materials are observed in the laboratory must be considerably higher than the maximum temperature to which these materials had been exposed in their previous geological history.[21] Our ESR investigation indicates that a temperature of about 150 °C must be attained before the conversion of the kerogen/asphaltene VO^{2+}-P into VO^{2+}-non-P occurs at a rate that can be observed in the laboratory (about 20 days). Therefore, we may hypothesize that if this conversion had occured in a particular geological material then this material had to have been exposed to much lower temperatures than 150 °C over a geological time scale (say, <100 °C).

Demineralized (Page and Windingstair) impsonite samples were examined by ESR. The examination revealed the presence of VO^{2+}-P in amounts comparable to those in the kerogens of the LL and Se rocks.[5] Kinetic parameters from our very recent pyrolysis experiments show that some asphalts can be completely converted into kerogen-like (amorphous) material at temperature of 70 °C (for < 100 days) up to 250 °C (for < 2 days) in the presence of air (O_2).[7,8] In the light of these experimental results, we are led to the view that the conversion of soluble asphaltic petroleums (including asphalt) into insoluble (kerogen-like) solid bitumen (such as impsonite/grahamite) had to occur through natural thermal kerogenization of asphaltic petroleums in the presence of air (O_2).[15]

Therefore, we can suggest that if the aerobic conversion of asphalt to impsonite/grahamite has occurred,[15] then the parent asphaltic petroleum had to have been exposed to temperatures much lower than 150 °C over the geological time scale (*e.g.*, < 100 °C).

The ESR spectra of the W. Kentucky coal samples studied were similar to the spectrum of VO^{2+}-non-P, Fig. 1c. However, in addition to the hyperfine coupling,

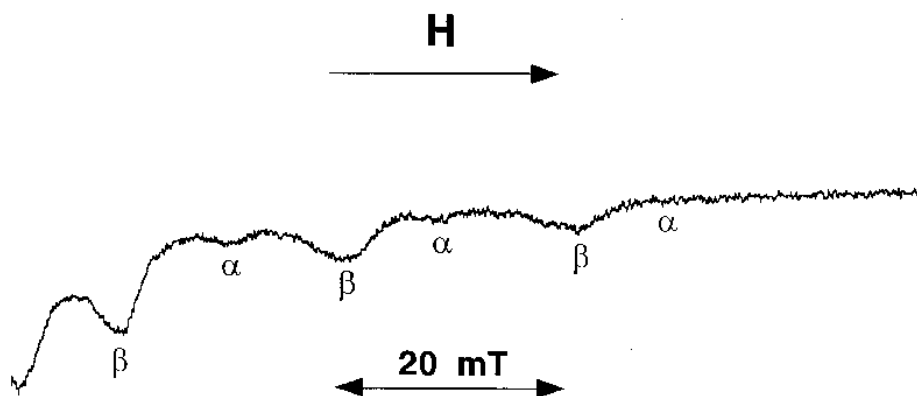Fig. 3. The high field portion of the X-band ESR spectrum (the W. Kentucky coal: the Millport mine): the VO^{2+}-P a) and the VO^{2+}-non-P b) signals.

each of the VO^{2+} lines of the spectra of the coal samples from some sites were either broadened or further split into a number of sublines. The presence of VO^{2+} subspestra is most obvious for the resonancies representing parallel orientations of the V=O axis with respect to the external magnetic field. In order to illustrate the complex pattern of VO^{2+} subspectra better, the high field portion of the X-band ESR spectrum of the Millport sample is shown in Fig. 3. This portion shows that each of the high-field signals from the same M_I transition is further split into two sets of subresonances. The most prominent features, belonging to the hyperfine lines from two different VO^{2+} subspectra, are labeled a and b; a is ascribed to the minor VO^{2+}-P and b to the predominant VO^{2+}-non-P. Finally, in contrast to the results for the LL/Se kerogens, VO^{2+}-non-P of the pyrolyzed W. Kentucky coal diminished after 6 h of laboratory heating at 250 °C in the presence of air O_2. The lower stability of VO^{2+}-non-P of the W. Kentucky coal over those of the LL/Se kerogens can be rationalized by their structural differences.

The origin of the VO^{2+}-non-P of the W. Kentucky No. 9 coal might at first sight seem relatively simple. The traditional view is that vanadylation (*i.e.* the formation of VO^{2+}-non-P) of the coal occurred during its peat-forming stage.[16] This view was advanced before the presence of VO^{2+}-P in W. Kentucky coal had been clearly established. At present, the senior author (P.I.P.) considers that the origin of the VO^{2+}-non-P of W. Kentucky coal is inextricably bound up with the subject of VO^{2+}-P. It is possible that the parent coal (or part of it) was originally a material rich in VO^{2+}-P which were converted into the coal/kerogen like material through near-surface oxygenic processes by natural heating at temperature ‡ 70 °C.[16] A more detailed discussion is beyond the scope of this paper, but will be published elsewhere.

CONCLUSION

Isothermal laboratory heating of the LL/Se kerogens at 250 °C for 1–20 days in the presence of air O_2 converts the kerogen VO^{2+}-P into VO^{2+}-non-P. A similar conversion is observed under the same experimental conditions for the asphaltenes extracted from the LL/Se rocks, and floating asphalt from the Dead Sea.

The samples of the W. Kentucky No. 9 coal (enriched with V) from six mines show the presence of predominantly VO^{2+}-non-P, similar to those generated through the oxygenic heat treatment of the kerogen/asphaltene materials described above.

И З В О Д

ВАЗДУШНА ОКСИДАЦИЈА КЕРОГЕНСКИХ/АСФАЛТЕНСКИХ ВАНАДИЛ ПОРФИР-ИНА: ЕЛЕКТРОНОСПИНСКА РЕЗОНАНТНА СПЕКТРОМЕТРИЈА

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Проучавано је термално понашање ванадил порфирина помоћу електроноспинске резонанције током загревања керогена изолованих из Ла Луна (Венецуела) и Серпиано

(Швајцарска) битуминозних стена, на 250 ºC, од 1 до 20 дана у присуству ваздуха. Током загревања керогена, ESR сигнал ванадил порфирина монотоно опада и постаје врло мали након 6 дана загревања. Упоредо са тим јављају се сигнали нових ванадилских врста, који после дужег загревања, доминирају у спектру. Претпостављено је да се секундарне ванадилске врсте формирају од ванадил порфирина. Примећено је слично претварање ванадил порфирина асфалтена издвојених из Ла Луна и Серпиано стена и плутајућег асфалта из Мртвог мора (Израел), под истим експерименталним условима. Упоре-ђивање спин-Хамилтонијанских параметара ванадил порфирина и новонасталих вана-дилских врста указује да су оне непорфиринског типа. Ради поређења, проучаван је угаљ из западног Кентакија (САД) обогаћен вандијумом (>400 ppm) из шест рудника. Сви узорци угља углавном садрже ванадил непорфиринска једињења слична онима која настају горе описаним лабораторијским загревањем керогена/асфалтена. Поред тога, неки од ових узорака садрже и мале количине ванадил порфирина.

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